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Methods for Level 2 Analysis by Organic Compound Category

Arthur D. Little, Inc.
Cambridge, MA

Prepared for

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16. ABSTRACT

The report gives Level 2 procedures, including results of a laboratory evaluation of detailed methods for analyzing organic chemicals in particular compound categories. The report, supplementing an earlier Level 2 procedures manual, provides an initial experimental data base as a resource for laboratories undertaking Level 2 studies. The Level 2 methods were designed to provide more detailed and more accurate data concerning specific compounds whose presence in the sample could be inferred on the basis of the categorical analysis of Level 1. A systematic laboratory evaluation of the methods for Level 2 analysis of each major category of organic compounds was conducted. Methods were evaluated using sets of model compounds spanning a range of molecular weights and boiling points in each category. Evaluation criteria included: detection limit, retention time, chromatographic resolution, and precison and accuracy of the method. Specific detailed Level 2 methods have been recommended for 25 categories of organic compounds. Most of the primary recommendations are based on packed-column gas-chromatography/mass-spectrometry, with alternative procedures suggested where appropriate for particular sample matrices or compound types. Analytical data using the specified example conditions are usually illustrated for each recommended method.

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Organic Compounds	Stationary Sources	07C
Analyzing	Level 2 Analysis	14B
Gas Chromatography		07D
Mass Spectrometry		

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ABSTRACT

The report gives Level 2 procedures, including results of a laboratory evaluation of detailed methods for analyzing organic chemicals in particular compound categories. The report, supplementing an earlier Level 2 procedures manual, provides an initial experimental data base as a resource for laboratories undertaking Level 2 studies. The Level 2 methods were designed to provide more detailed and more accurate data concerning specific compounds whose presence in the sample could be inferred on the basis of the categorical analysis of Level 1.

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I. SUMMARY

This handbook of Level 2 procedures presents the results of a laboratory evaluation of specific detailed methods for analysis of organic chemicals in particular compound categories. The report supplements the earlier Level 2 Procedures Manual[1] and provides an initial experimental data base as a resource for laboratories undertaking Level 2 studies. The Level 2 methods were designed to provide more detailed and more accurate data concerning specific compounds whose presence in the sample could be inferred on the basis of the categorical analysis of Level 1.

A systematic laboratory evaluation of the methods for Level 2 analysis of each major category of organic compounds was conducted. Methods were evaluated using sets of model compounds spanning a range of molecular weights and boiling points in each category. Evaluation criteria included: detection limit, retention time, chromatographic resolution, and precision and accuracy of the method.

Specific detailed Level 2 methods have been recommended for twenty-five categories of organic compounds. Most of the primary recommendations are based on packed column gas chromatography/mass spectrometry, with alternative procedures suggested where appropriate for particular sample matrices or compound types. Analytical data using the specified example conditions are usually illustrated for each recommended method.

The strategy for application of the recommended Level 2 methods to real environmental samples is illustrated by a partial Level 2 analysis of a combustion effluent sample. The Level 1 data on the sample are reviewed to illustrate the Level 1 to Level 2 transition process and decision criteria. The Level 2 analysis provided qualitative confirmation of compound classes, subcategories, and specific compounds identified at Level 1. Level 2 quantitative data agreed with expectations based on Level 1 chromatographable organics. However, comparison of the partial Level 2 data with the total quantity of organics found by Level 1 for this sample illustrates that additional types of analysis methods will need to be developed to make possible complete Level 2 analysis of the range of organics identifiable at Level 1.

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II. INTRODUCTION

This handbook of methods for Level 2 Analysis of organic materials represents a step in the development of a general methodology for chemical and biological assessment of environmental effects of industrial effluents. It is a supplement to the Level 2 Procedures Manual[1] for sampling and analysis of organics which was published in 1979. The Procedures Manual[1] presented concepts and general guidelines for Level 2 sampling and analysis. It also suggested specific analysis procedures that were considered to be appropriate for particular organic compound categories. This handbook presents the results of laboratory evaluations of the specific recommended analytical methods and provides an initial analytical data base as a resource for laboratories undertaking Level 2 studies.

A. Level 1/Level 2 in the Phased Approach

Both this handbook and the earlier Procedures Manual were prepared to support IERL/RTP's phase approach to the overall environmental assessment program. The Process Measurements Branch has developed a three-phased approach to sampling and analysis for environmental assessment. The philosophy of this approach, which has been described elsewhere[2] is briefly described here to provide a context for the present document.

Level 1, the first phase of sampling and analysis for environmental assessment, is designed to provide enough information about the composition of effluent and process streams to permit them to be ranked in order of priority with regard to probable environmental hazard. The Level 1 assessment is intended to: (1) provide preliminary environmental assessment data, (2) identify principal problem areas, and (3) formulate the data needed for ranking of energy and industrial processes, streams within a process, components within a stream, and classes of materials for further consideration in the overall assessment. The second phase of sampling and analysis effort, Level 2, is designed to provide additional information that will confirm and expand the information gathered in Level 1. The third phase, Level 3, involves quantitative monitoring of specific pollutants to provide information for control device design, development and evaluation.

The objective of a Level 2 study will be to obtain more detailed and accurate data about the composition of a particular process stream than is available in the context of a Level 1 study. The improved accuracy could be either primarily quantitative in terms of establishing a truly representative emission rate, or primarily qualitative in identifying organic species, or both.

Level 2 inquiries are expected to be directed primarily at the identification, quantification and confirmation of specific compounds whose presence could be inferred on the basis of the categorical analysis of Level 1.

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For example, Table 1 summarizes the results of Level 1 analysis of a SASS train sample from a ferroalloy process emission stream[3], upstream of any control device. Level 2 characterization of this emission source would include directed analysis of polycyclic aromatic hydrocarbons, shown by Level 1 to be the most abundant organic category present, to obtain compound-specific data. Specific Level 2 analyses would probably also be indicated for the heterocyclic nitrogen compounds, ketones and heterocyclic sulfur compounds. Within some compound categories, the Level 1/Level 2 transition might take the form of a decision to do a quantitative analysis for selected species known to be of particular concern. An example would be to conduct a specific analysis for benzene, since Level 1 shows aromatic hydrocarbons as a category. It might well be determined, however, that the emissions of aliphatic hydrocarbons and carboxylic acids are sufficiently low that no further information on these categories is required for Level 2 assessment of this source.

It is important to keep in mind that Level 1 organic analysis is not restricted to low molecular weight organics. In fact, many of the Level 1 studies performed to date[4] show that the distribution of organics in effluent streams tends to be biased towards higher molecular weight materials (Level 1 GRAV range[5]), rather than towards the lower molecular weight material (Level 1 TCO range[5])that can be analyzed by gas chromatography. Obviously, there is a need within the context of the overall environmental assessment program to have Level 2 procedures than can span the full molecular weight range of organics. However, the art of compound-specific analysis, especially quantitative analysis, of high molecular weight organic species in environmental samples is in its infancy. Development and evaluation of specific new methods for this purpose are beyond the scope of this handbook. Some possible approaches discussed in the Level 2 Procedures Manual[1] include: Fourier Transform infrared and nuclear magnetic resonance spectrometry, gel permeation chromatography and high resolution mass spectrometry.

Based on information available to date, it appears that mass spectrometric analysis of sample extracts, using the direct insertion probe, is an attractive approach to obtaining Level 2 information on the non-chromatographable GRAV range materials identified in Level 1 analysis. High resolution mass spectrometry (HRMS) can provide better qualitative information that available from the Level 1 low resolution mass spectrometry (LRMS). The quantitative estimates provided by Level 1 LRMS can be improved by applying the method of known addition to the LRMS (or HRMS) analysis for particular compounds suspected to be present at levels of concern.

B. Scope of this Handbook

If Level 1 analysis shows a category to be present at concentrations that exceed the emission level criteria for a particular environmental assessment, then Level 2 information will generally be needed to determine whether/which particular members of that category are present and to obtain better quantitative data. For most organic compound categories,

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TABLE 1

Summary of Level 1 Data for a Ferroalloy Process Emission Sample

Category	Source Concentration mg/m^3
Aliphatic Hydrocarbons	6.9
Aromatics	3.7
Fused Aromatic Hydrocarbons (PAH)	
mw <216	380
mw >216	450
Heterocyclic S	37
Heterocyclic N	80
Ketones	67
Alcohols	∿0.1
Esters	0.9
Carboxylic Acids	4.3
Total	1030

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the specific organic compounds that are known to be of concern with regard to potential impacts on health and/or the environment are the lower molecular weight members of the category, for which toxicological and ecological effects data exist. For example, the MEG list[6] focuses almost exclusively on compounds with molecular weights less than 300. Therefore, it seemed clear that the most immediate need was to develop and evaluate Level 2 methods that are applicable to this molecular weight range. The analytical methods presented in this handbook, which were selected primarily to meet that need, therefore rely heavily on gas chromatography/mass spectrometry (GC/MS) as a broad but selective technique for analysis of low to moderate molecular weight organics.

This handbook presents the results of a laboratory investigation and evaluation of the set of detailed procedures for analysis of organic compounds by category recommended in the February 1979 Level 2 Procedures Manual. Those recommendations had evolved, based on careful review of literature and discussions with other workers experienced in the chemical anlaysis of organic pollutants, from a list of possible procedures in the Interim Level 2 Manual[1]. The laboratory evaluation of the recommended procedures had two objectives:

- To determine whether the original recommendations were appropriate with or without minor modifications and,
- To provide appropriate analytical data to the users of the Level 2 analytical techniques.

The experimental approach is described in Section III and experimental detail for each method evaluated is provided in Section IV of this handbook. The basic approach was to evaluate each method using a test mixture of model compounds representative of that category. Criteria for method evaluation included: lower limits of analysis, analysis time, chromatographic resolution, precision and accuracy. The result of these experiments, presented in Section IV, are a set of analytical procedures with supporting data available, including specific analytical conditions, chromatographic retention times, lower limits of analysis, and precision and accuracy data. Relevant data from other sources were also included when available.

This handbook is intended for use, in conjunction with the Level 2 Procedures Manual, by experienced research chemists who are presumed to be familiar with environmental sampling and analysis, with the Level 1 procedures, and with the objectives of the phased approach. Chemists with this necessary background understanding will recognize that the detailed recommended analytical conditions, which were optimized for a particular representative set of compounds in a category, may require minor or substantial modifications to be applicable to other sets of compounds or to some complex sample matrices. In planning the Level 2 analysis of an environmental sample, the analyst must consider all of the available data in order to select the optimum set of methods

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from the procedures of Section IV. In particular, the detailed reports of the Level 1 LRMS, LC and IR analyses should be reviewed, since they contain valuable information on volatility and molecular weight ranges of sample components and, in many cases, also indicate the specific organic compounds that led to the Level 1 category identification(s). This will provide valuable guidance on selection of GC conditions and appropriate compounds for method calibration, as well as indicate the nature of potential interferences. To illustrate several important aspects of the application of the Level 2 procedures to complex environmental samples, Section V of this handbook presents an example, with supporting rationale, of Level 2 analysis of a real sample starting with the Level 1 data.

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III. EXPERIMENTAL APPROACH

This section describes the overall experimental program that was employed for evaluation of the Level 2 procedures for organic compounds by categories. Details of the experimental work, including instruments and detectors used and model compounds tested, are presented in the discussion of each method in Section IV.

The objective of this work was to evaluate the analytical procedures recommended for specific organic compound categories in the manual, EPA/IERL-RTP Procedures for Level 2 Sampling and Analysis of Organic Materials[1]. Those procedural recommendations were based on work previously reported in the literature which seemed to be reliable and applicable to Level 2 needs and, also, on consultation with other laboratories working on related projects for EPA/IERL-RTP, and on limited experimental work to address the adequacy of a few of the procedures. The laboratory evaluation of recommended procedures described in this report (Section IV), was a systematic study of the methods for twenty-five major categories of organic compounds.

The level of laboratory activity invested in a given category-specific method varied according to the extent and reliability of the existing information. For some categories of compounds, the analytical methods were fairly well established and a good general analytical data base existed. In these cases, the experimental work was focused on the analytical finish to verify that the specific conditions in the recommended procedure were appropriate for analysis of a range of compound types within that category. Available data on sample preparation steps and analyte recoveries were reviewed and summarized along with the analytical data. In several cases where analytical procedures were less firmly established, both sample preparation steps and the analytical finish were experimentally evaluated in this work. Finally, method development activity was initiated and new methods proposed for a few categories for which no satisfactory method had been documented previously[1,6].

For each method evaluation a set of about five to twelve example compounds from the category in question was chosen. The specific chemicals selected were generally those with high DMEG values (low toxicity) to minimize the potential for worker exposure to the more harmful materials. An effort was made to span the range of molecular weights and/or boiling points of compounds to which the method might be applicable, although very high molecular weight species (MW > 300) were generally not included in the set.

Gas chromatography/mass spectrometry (GC/MS) was the method recommended[1,6] for most categories. The specific chromatographic conditions for these GC/MS methods were initially evaluated using an alternative detector; flame ionization detection (FID), electron capture detection (ECD), or alkali flame ionization detection (AFID). This method was cost effective and also served to verify the appropriateness of the alternative detector recommended for each category.

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The method evaluation criteria included considering the detection limit. An acceptable method was required to have a lower limit of analysis, at least as low as one-half of the expected level of environmental concern. The DMEG concentration values and an assumption of 10 L water sample or 30 m^3 air sample were used to estimate the appropriate target detection limits in each case. The value that has been reported as a detection limit for each component is the smallest amount injected on column that was found to produce a clearly discernible GC (or HPLC) peak with acceptable peak shape, using the revised recommended procedure for a test mixture. This criterion, rather than a specified signal-to-noise ratio, has been used in the interest of defining a conservative, but realistic, estimate of the lower range of applicability of the methods for quantitative analysis. The "detection limit" values thus reported include criteria of detector sensitivity and chromatographic peak shape and intensity. Lower absolute detection limits may be achievable in some sample matrices.

Other evaluation criteria applied to the recommended methods included a reasonable analysis time, which was considered to be about 30 minutes or shorter retention time for individual compounds and about one hour maximum sample-to-sample turn-around time. It was necessary to verify that the column and conditions provided adequate chromatography to resolve the compounds known or suspected to be primary interest within the category. The precision and accuracy associated with the overall procedure, including both sample preparation and analytical finish, were also evaluated.

The result of the laboratory evaluation is the set of analytical methods presented in Section IV along with supporting analytical data. The method descriptions in Section IV include specific analytical conditions, chromatographic retention times, lower limits of analysis, and precision and accuracy data for the model compounds tested in each category.

IV. LEVEL 2 METHOD RECOMMENDATIONS

The Level 2 methods presented in this report have been designed to provide compound specific information, both qualitative and quantitative, for the categories of organic compounds that were identified as present at significant concentration by Level 1 (or equivalent) techniques. The Level 2 methods, like the Level 1 reporting categories, are organized according to the categorization scheme of the MEG list[3].

Level 2 methods are recommended for 25 categories of organic species. The recommended method, as well as alternative methods, are given for each of these 25 categories. Some of the Level 2 methods for each category of organics are subdivided by boiling point ranges and polarity. This was done because it was not always possible to have one method for all the species in a particular category. Further, alternative methods are recommended should the primary recommendation not work for a particular sample matrix or organic compound, or if necessary equipment is not available.

Method evaluation data are also included with the method recommendations by category. Most of the analytical finishes and some sample preparation procedures were evaluated in the laboratory, although a few of the methods, listed as tentative, have been included without laboratory evaluation. Where possible, data available from other sources are included to support and illustrate the method recommendations.

A summary of the methods for each category is presented in Table 2. These methods are the primary recommendations; the alternative methods can be found by category. The analytical conditions specified for each of the methods should be considered as guidelines for Level 2 analysis. These example conditions provide the analyst with a reference point for the Level 2 analysis. For example, the gas chromatography column temperature program may have to be modified in order to resolve particular organic species in a sample. Analytical data using the specified conditions are usually included with each method recommended. The relative retention time data given for a series of organic compounds representative of the category provide guidance as to whether modifications in GC column temperature programming are necessary for the particular problem at hand.

The Level 2 methods are optimized for a particular category of organics. Therefore, any single one of these methods is not directed towards analyzing all the organic species in a sample. Where possible, the same method is recommended for a number of organic categories in order to limit the total number of methods which may be needed to analyze a sample.

As can be seen in Table 2, most of the methods use packed gas chromatography (GC) columns. The Level 2 methods incorporate specific GC packings. In many cases, equivalent GC packings are available and some of these are discussed in Appendix A. Overall, the recommended packed GC columns have been found to have adequate resolution to analyze the organic compounds in an environmental sample. However, when complex environmental samples are being analyzed, better resolution of the constituents in a sample may be necessary for a Level 2 analysis. Capillary GC columns offer higher resolution capabilities, however, the capacity in a capillary GC column is not as great as that attainable by conventional packed GC columns. A discussion concerning capillary GC columns for Level 2 studies is given in Appendix B.

some recommended capillary GC columns for Level 2, by MEG category

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TABLE 2

Method Summary*

Gas Chromatography/Mass Spectroscopy (GC/MS)

Category Number	Category Name	GC Packing
2	Alkyl Halides	
	A. BP < 150°C	0.2% Carbowax 1500, 80/100, Carbopack C
	B. BP > 150°C	3% SP 2250, 80/100 SP
7B	Ketones	0.1% SP 1000, 80/100, Carbopack C
8A,B	Carboxylic Acids Monoacids to C_5	60/80 Carbopack B, 3% Carbowax 20M; 0.5% H_3PO_4
8C	Amides	3% Dexsil 400, 100/120 SP
8D	Esters	3% SP 2250, 100/120 SP
9	Nitriles	3% SP 1000, 100/120 SP
10	Amines	4% Carbowax 20M on Carbopack B + .8% KOH
12	Nitrosamines	3% SP 2100, 100/120 SP
13	Mercaptans, Sulfides and Disulfides BP > 60°C	3% SP 1000, 100/120 SP
14B	Sulfoxides	3% SP 1000, 100/120 SP

*Primary recommended methods are listed, alternative methods can be found by category.

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TABLE 2 (Continued)

Method Summary*

Gas Chromatography/Mass Spectroscopy (GC/MS)

Category Number	Category Name	GC Packing
15	Benzene and Substituted Benzene Hydrocarbons	
	A. BP 80°C-200°C	0.1% SP 1000, 80/100 Carbopack C
	B. BP > 110°C	3% SP 2250, 100/120 SP
16	Halogenated Aromatic Compounds	3% SP 2250, 100/120 SP
17	Aromatic Nitro Compounds	3% SP 2250, 100/120 SP
18,19,20	Phenols, Halophenols, Nitrophenols	1% SP 1240 DA, 100/120 SP
21,22	Polynuclear Aromatic Hydrocarbons	3% Dexsil 400, 100/120 Chromosorb W AW
23	Heterocyclic Nitrogen Compounds	3% Dexsil 400, 100/120 SP
24	Heterocyclic Oxygen Compounds	3% SP 1000, 100/120 SP
25	Heterocyclic Sulfur Compounds	
	A. BP 80°C-200°C	0.1% SP 1000, 80/100 Carbopack C
	B. BP > 110°C	3% SP 2250, 100/120 SP

*Primary recommended methods are listed, alternative methods can be found by category.

TABLE 2 (Continued)

Method Summary*

Gas Chromatography/Flame Ionization Detection (GC/FID)

Category Number	Category Name	GC Packing
1	Aliphatic Hydrocarbons	
	A. BP < 50°C	Durapak n-Octane/Porasil C, 100/120
	B. BP 50°C-250°C	10% SP 2100, 100/120 SP
	C. BP > 150°C	3% Dexsil 400, 100/120 Chromosorb W AW
3,4	Ethers, Halogenated Ethers	3% SP 1000, 100/120 SP
5	Alcohols	
	A. BP < 200°C	0.1% SP 1000, 80/100 Carbopack C
	B. BP > 200°C	3% SP 2100, 100/120 SP
6	Glycols, Epoxides	3% SP 1000, 100/120 SP

*Primary recommended methods are listed, alternative methods can be found by category.

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TABLE 2 (Continued)

Method Summary*

High Performance Liquid Chromatography

Category Number	Category Name	HPLC Packing	Detector
7A	Aldehydes	Zorbax ODS (DNPH derivatives)	UV at 254 nm
8A,B	Carboxylic Acids	µBondapack/C_{18}	UV at 210 nm, at 254 nm
14A	Sulfonic Acids	Lichrosorb SI60, Silanized	UV at 254 nm

Colorimetric Techniques

Category Number	Category Name	Derivative
11	Azo Compounds, Hydrazine, and Derivatives	Phosphomolybdic Acid

*Primary recommended methods are listed, alternative methods can be found by category.

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Aliphatic Hydrocarbons (MEG Category 1)

The compounds included in the aliphatic hydrocarbons category are divided into three subcategories:

Alkanes and Cyclic Alkanes (No. 1A),
Alkenes, Cyclic Alkenes and Dienes (No. 1B), and
Alkynes (No. 1C).

The recommended analytical method for this category is gas chromatography with flame ionization detection (GC/FID). Gas chromatography columns are recommended for species within particular boiling point ranges. These boiling point ranges overlap, therefore, permitting flexibility in the choice of a GC column.

The flame ionization detector is not a selective or specific detector, therefore, care must be taken when identifying the GC peaks as aliphatic hydrocarbons during a Level 2 analysis. If this category is a major concern, once identities have been assigned using retention time data from the GC/FID analysis, gas chromatography/mass spectroscopy (GC/MS) may be used for confirmation. Low ionization voltages using electron impact (EI) mass spectrometry or soft ionization techniques, e.g., chemical ionization mass spectrometry, may be used in order to obtain molecular ions. This information, combined with fragmentation patterns obtained from EI-MS at typical ionization voltages, is useful when assigning identities.

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ALIPHATIC HYDROCARBONS - (MEG CATEGORY 1)

Recommended Method

Recommended Method: GC/FID

A. Species with Boiling Points up to 50°C

Column: Durapak n-Octane/Porasil C, 100/120 mesh, 3m x 2mm glass

Note: Reference 7 suggests a complementary column if necessary.

Example Conditions: Carrier Gas: 25 mL/min., Helium

Column Temperature: 30°C (8 min.) $\xrightarrow{6°C/min.}$ 135°C

Flame Ionization Detector: 200°C

Injector 150°C

Lower Limit of Analysis: 1 ng injected - Alkanes and Alkenes (equivalent to 0.5 ppm in gas sample) 15 ng injected - Alkynes (equivalent to 15 ppm in gas sample)

B. Species with Boiling Points in the Range 50°C to 250°C

Column: 10% SP 2100 on 100/120 mesh Supelcoport, 2m x 2mm glass

Example Conditions: Carrier Gas: 20 mL/min., Helium

Column Temperature: 30°C (4 min.) $\xrightarrow{6°C/min.}$ 200°C

Flame Ionization Detector: 250°C

Injector: 225°C

Lower Limit of Analysis: 2 ng injected (except long injected for compounds with b.p. 80°C when CH_2Cl_2 is used as the solvent).

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C. Species with Boiling Points greater than 150°C

Column: 3% Dexsil 400 on 100/120 mesh Chromosorb WAW, 3m x 2mm glass

Note: Silanized supports, e.g., Supelcoport, may be used when operating at temperatures less than 350°C. Silane groups bleed off at 350°C.

Example Conditions: Carrier Gas: 20 mL/min, Helium

Column Temperature: 65°C
↓ 8°C/min.
400°C

Lower Limit of Analysis: 5 ng injected

Suggested Alternative Methods

1. For resolution of very complex mixtures, the following capillary column can be used:

   Column: SP 2100, 50 meters

   Example Conditions: Carrier Gas: 20 cm/sec., Helium

   Column Temperature: 50°C
   ↓ 2°C/min.
   200°C

2. For separation of very high boiling species, 1% Dexsil 400 on 100/120 Chromosorb WAW, 0.5m x 2mm glass

3. GC/MS can be used for confirmation.

4. GC/MS will give detection limits of about 100 to 500 ng injected.

Reference

7. Saha, N.C., S.K. Jain and R.K. Dua, "A Generalized and Easily Adaptable Gas Chromatographic Method for the Analysis of Gaseous Hydrocarbons," J. Chromatograph. Science, 15, 323 (1978).

ALIPHATIC HYDROCARBONS - (MEG CATEGORY 1)

Method Evaluation

A. Species with Boiling Points up to 50°C

The analytical method[8] originally recommended for aliphatic hydrocarbons with boiling points up to 50°C in the Level 2 Sampling and Analysis Manual was:

Column: Durapak n-Octane/Porasil C, 100/120 mesh,
2m x 2mm stainless steel or glass

Example Conditions: Flow Rate: 25 mL/min.
Column Temperature: 25°C Isothermal

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph fitted with a 1 mL gas sample loop. A 3m, instead of the recommended 2m x 2mm Durapak n-Octane/Porasil C 100/120 mesh GC column, was used for the analytical finish evaluation. The Durapak n-Octane/Porasil C column was conditioned overnight at 200°C.

Three aliphatic hydrocarbon gas mixtures, n-Alkanes (C1-C6), n-Alkenes (C2-C6), and Alkynes (C2-C4) in nitrogen (purchased from Supelco, Inc.), were used for the evaluation. Each mixture (in N_2) was chromatographed on the Durapak n-Octane/Porasil C GC column using the recommended conditions to determine whether the individual compounds were adequately resolved. The original method recommended isothermal operation at 25°C, however, column temperature programming was more appropriate for these test mixtures. GC column temperature programming from 30°C (isothermal 8 min.) to 135°C at 6°C/min was experimentally determined to be adequate for resolving the aliphatic hydrocarbons.

A test mixture (Mixture 1) in N_2 was prepared consisting of the alkanes, alkenes, and alkynes, listed in Table 3, to give concentration levels indicated. All gas dilutions were made using a 2000 mL glass dilution bulb and gas tight syringes. The test mixture was chromatographed on the n-Octane/Porasil C GC column using the revised conditions. The alkynes in the test mixture could not be satisfactorily resolved from the alkanes and alkenes (Figure 1), therefore, the alkynes were evaluated in a separate analysis to determine the lower limit of analysis for these species (Table 4, Figure 2).

It was necessary to determine the GC peak retention time of each aliphatic hydrocarbon in the three categories, i.e., alkanes, alkenes, and alkynes. The retention times for aliphatic hydrocarbons in a mixture generally increase with increasing boiling point. Vapors of pentane and hexane were chromatographed separately on the Durapak n-Octane/Porasil C GC column using the revised conditions, to ascertain that this was true. The retention times, 13.65 min. for pentane and 19.88 min. for hexane, were identical with the retention times for the peaks in the mixture that had been assigned to these compounds on the basis of their boiling points. Therefore, the order of elution of the aliphatic hydrocarbons from the GC column does increase with increasing boiling points. It was assumed that this boiling point order of elution would also be within the alkene and alkyne categories. The retention times of the aliphatic hydrocarbon GC peaks are given in Tables 3 and 4. Based on these data for a 3m column, the recommended 2m column would probably also be adequate for separation.

The lower limit of analysis for each aliphatic hydrocarbon was determined. Three test mixtures of alkanes and alkenes in air were prepared at the concentration levels listed in Table 5. These test mixtures were chromatographed on the n-Octane/Porasil C GC column using the revised conditions. Each compound was readily detectable at less than 1 nanogram injected on column (equivalent to approximately 0.5 ppm in gas sample).

The alkyne mixture (Table 4, Mix 2), was chromatographed separately on the n-Octane/Porasil C GC column at 30°C isothermal. The revised conditions could also be used since there is an 8 minute pretemperature hold at 30°C prior to the temperature programming. The lower limits of analysis for the individual alkynes were considerably higher than those found for the alkanes and alkenes. Each alkyne in the mixture was readily detected at the concentrations listed in Table 4 (15-38 ng/mL, equivalent to approximately 15 ppm in a gas sample).

TABLE 3

Analytical Data for Aliphatic Hydrocarbons with Boiling Points up to 50°C

(MEG Category 1)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC[1] Peak No.	Mix 1 Conc. (ng/mL)	RRT[2]
1C	Acetylene	C_2H_2	26.04	-75.0	1	15.4	0.19
1A	Methane	CH_4	16.04	-162.0	2	6.37	0.19
1A	Ethane	C_2H_6	30.07	-88.5	3	13.4	0.27
1B	Ethylene	C_2H_4	28.05	-102.0	3	11.1	0.27
1C	Propyne	C_3H_4	40.07	-23.0	3	24.7	0.27
1A	Propane	C_3H_8	44.11	-42.0	4	18.6	0.44
1C	1-Butyne	C_4H_6	54.09	9.0	4	31.2	0.44
1B	Propene	C_3H_6	42.08	-48.0	5	16.5	0.63
1A	Butane	C_4H_{10}	58.13	0	6	24.5	1.00
1C	2-Butyne	C_4H_6	54.09	27.0	6	36.7	1.00
1B	1-Butene	C_4H_8	56.12	-6.5	7	18.6	1.63
1A	Pentane	C_5H_{12}	72.15	36.0	8	31.3	2.25
1B	Pentene	C_5H_{10}	70.14	30.0	9	28.7	2.71
1A	Hexane	C_6H_{14}	86.18	69.0	10	34.9	3.28
1B	1-Hexene	C_6H_{12}	84.16	63.5	11	36.5	3.58

---

[1] GC peak numbers refer to Figure 1.

[2] Relative Retention Times (relative to butane, RT = 6.1 minutes)

Sample: 1 mL Mix 1 alkanes, alkenes, and Alkynes in N_2

Column: Durapak n-Octane/Porasil C, 100/120, 3m x 2mm glass

Carrier Gas: 25 mL/min., Helium

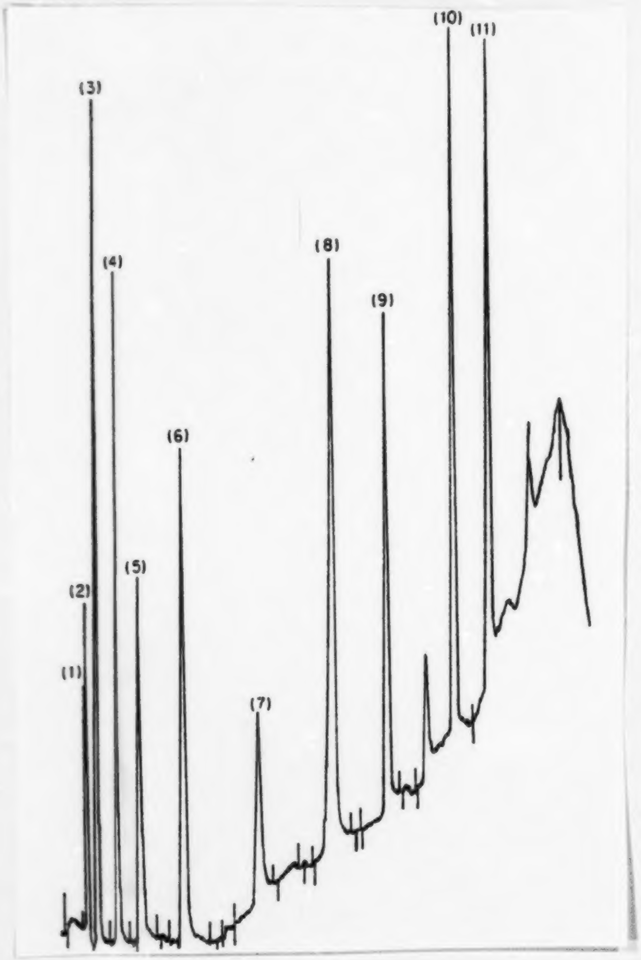
Column Temperature: 30°C (8 min.) $\xrightarrow{6°C/min.}$ 135°C

FID Temperature: 200°C

Injector Temperature: 150°C

Attenuation Range: 1×10^{-11} amps/mV

Chart Speed: 0.5 cm/min.



(GC peak numbers refer to Table 3)

Figure 1. Gas Chromatogram of Aliphatic Hydrocarbons - Alkanes, Alkenes, and Alkynes (boiling points ≤ 50°C)

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TABLE 4

Analytical Data for Alkynes with Boiling Points up to 50°C

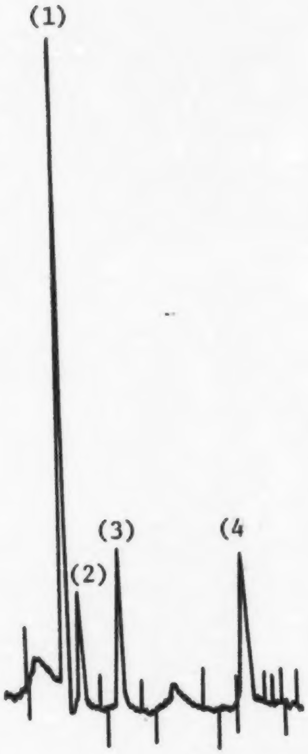
(MEG Category 1)

MEG Category No.	Compound	BP (°C)	GC[1] Peak No.	Mix 2 Conc. (ng/mL)	RRT[2]
1C	Acetylene	-75.0	1	15.4	0.40
1C	Propyne	-23.0	2	24.7	0.58
1C	1-Butyne	9.0	3	31.2	1.00
1C	2-Butyne	27.0	4	36.7	2.35

---

[1] GC peak numbers refer to Figure 2.

[2] Relative Retention Times (relative to Butyne, RT = 2.73 min)



Sample: 1 mL mix 2 alkynes in N_2

Column: Durapak n-Octane/Porasil C, 100/120 mesh
3m x 2mm glass

25 mL/min., Helium

Column Temperature: 30°C isothermal

FID Temperature: 200°C

Injector Temperature: 150°C

Attenuation Range: 4×10^{-12} amps/mV

Chart Speed: 0.5 cm/min.

(GC peak numbers refer to Table 4)

Figure 2. Gas Chromatogram of Alkynes with Boiling Points up to 50°C

TABLE 5

Concentration Data for Test Mixtures of Aliphatic Hydrocarbons with Boiling Points up to 50°C

(MEG Category 1)

MEG Category No.	Compound	Mix 3 Conc. (ng/mL)	Mix 4 Conc. (ng/mL)	Mix 5 Conc. (ng/mL)
1A	Methane	6.37	3.2	0.32
1A	Ethane	13.4	6.7	0.67
1B	Ethene	11.1	5.6	0.56
1A	Propane	18.6	9.3	0.93
1B	Propene	16.5	8.3	0.83
1A	Butane	24.5	12.3	1.2
1B	1-Butene	18.6	9.3	0.93
1A	Pentane	31.3	15.6	1.6
1B	1-Pentene	28.7	14.3	1.4
1A	Hexane	34.9	17.5	1.8
1B	1-Hexene	36.5	18.3	1.8

B. Species with Boiling Points in the Range 0°C to 200°C

The analytical method originally recommended for aliphatic hydrocarbons with boiling points in the range 0°C to 200°C in the Level 2 Sampling and Analysis Manual was:

Column: 3% SP 2100 on 100/120 Supelcoport
3m x 2mm glass or stainless steel

Conditions: Flow Rate: 20 mL/min.

Column Temperature: 50°C
↓ 6°C/min.
200°C

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph. A 3% OV-101 on 80/100 mesh Supelcoport GC column was substituted for the recommended 3% SP 2100 on 100/120 mesh Supelcoport. OV-101 is a 100% dimethyl silicone liquid phase and is equivalent to SP 2100 as indicated by identical McReynolds' constants. The 3% OV-101 column used was conditioned overnight at 320°C.

A test mixture of the aliphatic hydrocarbons listed in Table 6 was prepared in methylene chloride. This test mixture was chromatographed on the 3% OV-101 GC column, using the recommended conditions, to determine whether the individual compounds were adequately resolved. The original method recommended a column temperature program from 50°C to 200°C at 6°C per minute.

Under these conditions, aliphatic hydrocarbons with boiling points below about 90°C were not adequately resolved from the methylene chloride solvent front. This is not a serious intrinsic method drawback because organic species in this low boiling point range are normally sampled and analyzed as gases (glass bulb, thermal desorption of Tenax sample or purge and trap). Species with boiling points below 100°C would therefore be introduced to the GC in a solvent-free mode.

It was decided to determine experimentally whether slight modifications of column temperature program and/or column liquid phase loading would suffice to resolve the volatile aliphatics from the solvent and from each other. The column temperature program was changed to 30°C (hold 3 min.) to 200°C (hold 5 min.) at 6°C/min. This change was not sufficient to resolve the lower boiling compounds from the solvent peak. Therefore, a 10% OV-101 on 100/120 mesh Supelcoport column was studied. This column was found to be adequate for resolution of aliphatics over the range of 50°C to 250°C boiling point. Because of its broad applicability to both gases and vapors, the 10% OV-101 column was used for the detailed method evaluations. Its adequacy for species with boiling points less than 50°C was not evaluated in this study.

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It was necessary to determine the GC peak retention time of each aliphatic hydrocarbon compound in the test mixture. The retention times were determined by chromatographing a solution of each compound, using the revised recommended conditions. Retention times for each of the aliphatic hydrocarbon compounds in the test mixture are presented in Table 6. A representative gas chromatogram is presented in Figure 3. Three compounds, cyclooctane, 1,5-cyclooctadiene, and 1-nonyne, were not resolved. In GC/MS analysis, appropriate ions might be monitored by mass spectroscopy to distinguish the three compounds, if necessary, although aliphatics tend to have weak parent ions.

The detection limit for each aliphatic hydrocarbon compound was determined. Four test mixtures of the aliphatic hydrocarbon compounds were prepared in methylene chloride at concentration levels corresponding to 50 ng/μL, 10 ng/μL, 5 ng/μL and 2 ng/μL of each compound. The aliphatic hydrocarbon compounds with boiling points above 100°C were easily detected at 2 ng injected on column. The aliphatic hydrocarbon compounds with boiling points below 80°C were not resolved from the methylene chloride solvent GC peak at 2 ng injected. Aliphatic hydrocarbon compounds with boiling points less than 80°C were detected and reasonably resolved from the solvent GC peak at 10 ng injected on column.

TABLE 6

Analytical Data for Aliphatic Hydrocarbons with Boiling Points 0°C to 250°C

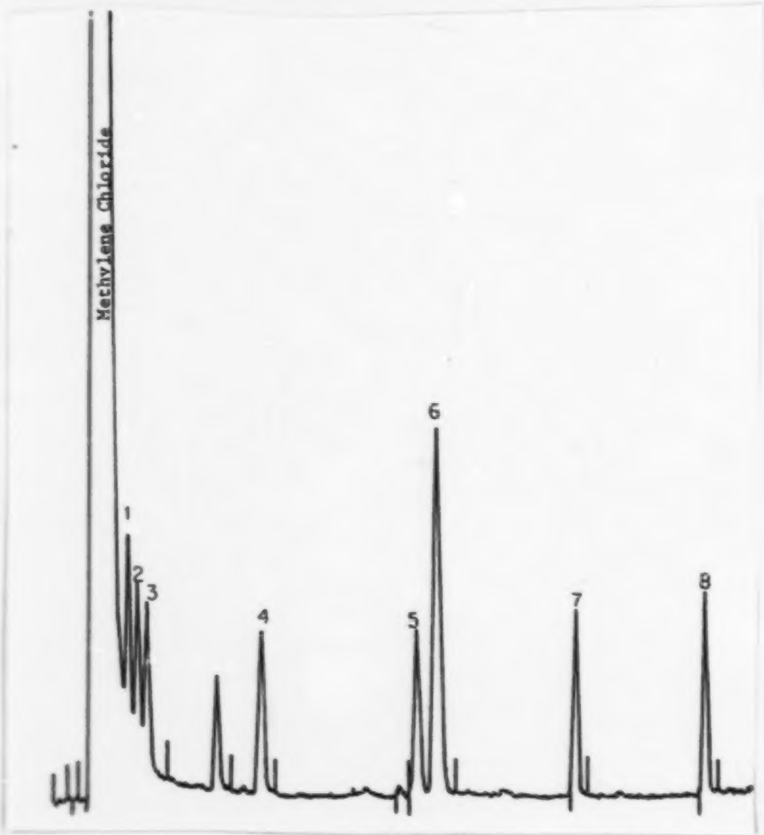
(MEG Category 1)

MEG Category No.	Compound	Composition	MW	BP (°C)	GC[(a)] Peak No.	RRT[(b)]
1B	1,5-Hexadiene	C_6H_{10}	82	60	1	0.23
1B	1- Hexene	C_6H_{12}	84	64	2	0.26
1A	Hexene	C_6H_{14}	86	69	3	0.28
1A	Methylcyclohexane	C_7H_{14}	98	101	4	0.59
1B	Cyclooctene	C_8H_{14}	110	145-146	5	1.00
1A	Cyclooctane	C_8H_{16}	112	149	6	1.05
1B	1,5-Cyclooctadiene	C_8H_{12}	108	151	6	1.05
1C	1-Nonyne	C_9H_{16}	124	151	6	1.05
1A	Undecane	$C_{11}H_{24}$	156	196	7	1.42
1A	Tetradecane	$C_{14}H_{30}$	198	254	8	1.77

(a) Numbers refer to gas chromatogram, Figure 3.

(b) Relative Retention Times (relative to cyclooctene, RT = 14.8 min.

Sample:	50 nanograms of each aliphatic hydrocarbon compound in 1 μL methylene chloride
Column:	10% OV-101 on 100/120 mesh Supelcoport, 2m x 2mm stainless steel
Carrier Gas:	20 mL/min., Helium
Column Temperature:	30°C (4 min.) $\xrightarrow{6°C/min.}$ 200°C
Injector Temperature:	225°C
FI Detector Temperature:	245°C
Attenuation x Range:	4 x 10^{-11} amp/mV
Chart Speed:	0.5 cm/min.



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(GC peak numbers refer to Table 6)

Figure 3. Gas Chromatogram of Aliphatic Hydrocarbons with Boiling Points 0°C to 250°C

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C. Species with Boiling Points greater than 200°C

The analytical method originally recommended for aliphatic hydrocarbons with boiling points greater than 200°C in the Level 2 Sampling and Analysis Manual was:

Column: 3% Dexsil 400 on 100/120 mesh Supelcoport,
3m x 2mm glass or stainless steel

Example Conditions: 20 mL/min.

Column Temperature: 150°C
↓ 8°C/min.
400°C

Analytical data concerning the chromatography of aliphatic hydrocarbons was available from another program[9]. In this study, standards of aliphatic hydrocarbons with boiling points greater than 150°C were prepared in carbon disulfide. One µL aliquots of these standards were injected on a 3% Dexsil 400 GC column and chromatographed using the conditions presented in Figure 4. A representative gas chromatogram is given in Figure 4 and the appropriate analytical data is given in Table 7.

TABLE 7

Aliphatic Hydrocarbons with Boiling Points greater than 150°C

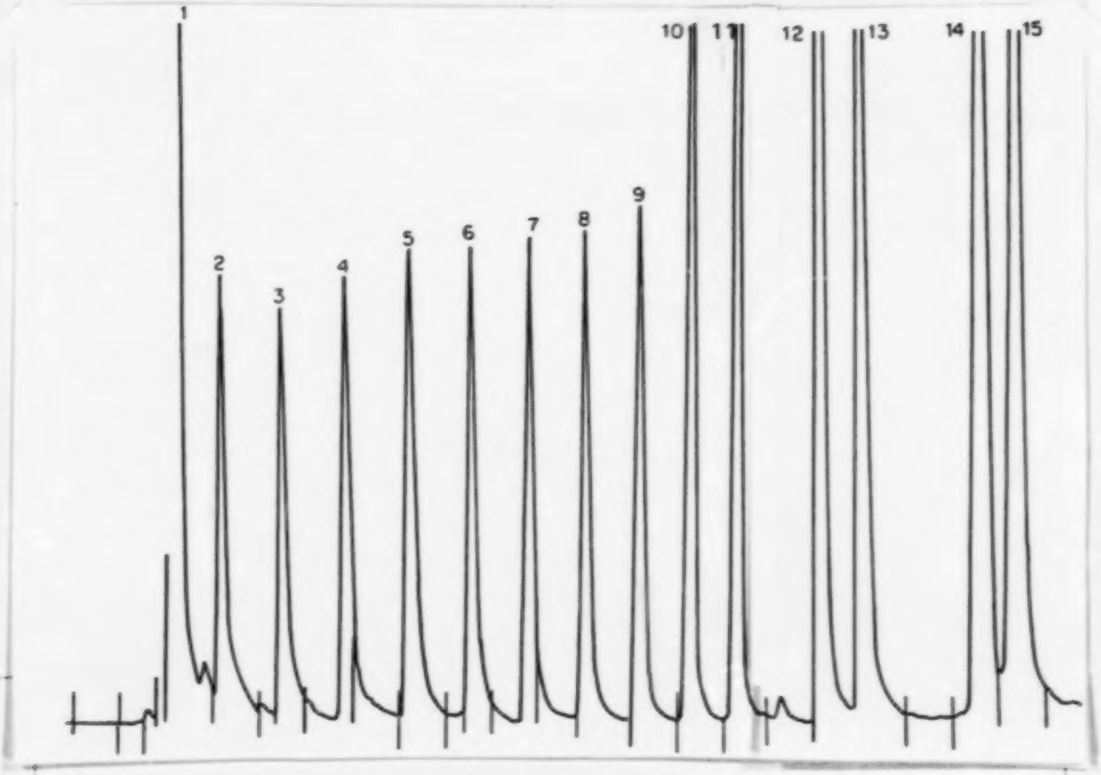
(MEG Category 1)

MEG Category No.	Compound	Composition	MW	BP (°C)	GC[a] Peak No.	RRT[b]
1A	Nonane	C_9H_{20}	128	151	1	.24
1A	Decane	$C_{10}H_{22}$	142	174	2	.34
1A	Undecane	$C_{11}H_{24}$	156	196	3	.45
1A	Dodecane	$C_{12}H_{26}$	170	216	4	.57
1A	Tridecane	$C_{13}H_{28}$	184	235	5	.68
1A	Tetradecane	$C_{14}H_{30}$	198	253	6	.79
1A	Pentadecane	$C_{15}H_{32}$	212	271	7	.90
1A	Hexadecane	$C_{16}H_{34}$	226	287	8	1.00
1A	Heptadecane	$C_{17}H_{36}$	240	302	9	1.09
1A	Octadecane	$C_{18}H_{38}$	254	317	10	1.18
1A	Nonadecane	$C_{19}H_{40}$	268	331	11	1.27
1A	Heneicosane	$C_{21}H_{44}$	296	356	12	1.43
1A	Docosane	$C_{22}H_{46}$	310	369	13	1.50
1A	Pentacosane	$C_{25}H_{52}$	352	402	14	1.71
1A	Hexacosane	$C_{26}H_{54}$	366	412	15	1.77

(a) Numbers refer to gas chromatogram, Figure 4.

(b) Relative Retention Times (relative to hexadecane, RT = 119 min.)

Sample:	**1 µL aliphatic hydrocarbon standard in carbon disulfide**
Column:	**3% Dexsil 400 on 100/120 mesh Supelcoport**
Flow Rate:	**30 mL/min.$^{-1}$, Nitrogen**
Column Temperature:	**65°C $\xrightarrow{10^\circ C/min.}$ 350°C**
Injector Temperature:	**230°C**
FI Detector Temperature:	**300°C**
Attentuation Range:	**4 x 16 x 10^{-10}**
Chart Speed:	**0.5 in. min.$^{-10}$**



(GC peak numbers refer to Table 7)

Figure 4. Gas Chromatogram of Aliphatic Hydrocarbon Compounds with Boiling Points greater than 200°C

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Alkyl Halides (MEG Category 2)

The compounds included in the alkyl halide category are divided into two subcategories:

Saturated Alkyl Halides (2A)
Unsaturated Alkyl Halides (2B)

The recommended analytical method for this category is gas chromatography/mass spectroscopy (GC/MS). Gas chromatography colums are recommended for species with boiling points less than 150°C and greater than 150°C.

ALKYL HALIDES - (MEG CATEGORY 2)

Recommended Method

Recommended Method: GC/MS

A. Species with Boiling Points less than 150°C

Column: 0.2% Carbowax 1500 on Carbopack C, 80/100 mesh Supelcoport, 2m x 2mm glass

Example Conditions: Carrier Gas: 30 mL/min., Helium

Column Temperature: 60°C

↓ 8°C/min.

160°C (isothermal, 20 minutes)

Lower Limit of Analysis: 5 ng injected

B. Species with Boiling Points greater than 150°C

Column: 3% SP 2250 on 80/100 mesh Supelcoport, 2m x 2mm glass

Example Conditions: Carrier Gas: 20 mL/min., Helium

Column Temperature: 100°C isothermal

Lower Limit of Analysis: 10 ng injected, except hexachlorocyclopentadiene - 100 ng injected

Suggested Alternative Methods

1. GC/ECD (same chromatographic conditions as in B above) is an alternative detection system for preliminary evaluation or for interference-free samples.

Electron Capture Detector:	275°C
Carrier Gas:	20 mL/min., 95% Argon/5% Methane
GC/ECD Lower Limit of Analysis:	10 picograms injected, except hexachloropentadiene - 150 picograms injected.

150

2. GC/Hall Electrolytic Conductivity Detection is an alternative detection system. This is the preferred conventional detector when purge-and-trap techniques are used for sample preparation (alkyl halides with boiling points less than 150°C).

ALKYL HALIDES - (MEG CATEGORY 2)

Method Evaluation

A. Species With Boiling Points in the Range 20°C to 200°C

The analytical method originally recommended for alkyl halide compounds (MEG Category 2) with boiling points between 20°C and 200°C in the Level 2 Sampling and Analysis manual was:

Column:	0.1% SP 1000 on Carbopack C, 80/100 mesh 2mm x 2m glass or stainless steel	
Example Conditions:	Flow Rate:	20 mL/min.
	Column Temperature:	175°C isothermal

The analytical finish for this category was evaluated using gas chromatography/electron capture detection (GC/ECD). The instrument used was a Hewlett Packard 5840 Gas Chromatograph. The recommended GC column, 0.1% SP 1000 on Carbopack C, was conditioned overnight at 200°C. A test mixture was prepared consisting of pentachloroethane (b.p. 162°C) and hexachloroethane (b.p. 186°C) in hexane. Hexane was chosen as the solvent in this analysis, due to its low response characteristics for GC/ECD analysis.

The test mixture was chromatographed on the 0.1% SP 1000, Carbopack C GC column, using the recommended conditions to determine whether the individual compounds were adequately resolved.

The hexane solvent chromatographed poorly on the column resulting in excessive tailing of this GC peak. This excessive tailing would interfere with the low boiling alkyl halide GC peaks. Further, the GC peaks attributable to hexachloroethane and pentachloroethane were quite broad. The detection limits for these compounds using GC/ECD were expected to be in the picogram range. However, poor chromatography resulted in the detection limits for the alkyl halide compounds in the nanogram range.

The demonstrated poor chromatography of hexachloroethane and pentachloroethane on the 0.1% SP 1000 on 80/100 Carbopack C GC column has necessitated recommendation of an alternative column.

In another program[10], a 0.2% Carbowax 1500 on 80/100 Carbopack C GC column is routinely being used to analyze alkyl halide compounds in the boiling point range of interest. In this program, GC/MS is used for the analysis. A calibration standard containing a mixture of compounds including twenty-seven alkyl halide compounds in methanol were chromatographed on the 0.2% Carbowax 1500 80/100 Carbopack C GC column using the example conditions. A representative total ion plot is presented in Figure 5. The appropriate analytical data is given in Table 8. The compounds which are not resolved in the total have sufficiently different

5 before 8

analytical ions such that the GC peak attributable to one of the compounds is ignored. For example, benzene and trichloroethylene co-elute. The analytical ions used to identify trichloroethylene are m/z 130, 132, 95, and 97; while the benzene ions are m/z 78, 77, 52, and 51. For this particular example, if a halide specific detector were used benzene would not be detected, therefore, the lack of resolution would not pose a problem.

Evidence concerning the precision and accuracy of the GC/MS method for the analysis of alkyl halide compounds is available from the results obtained from the same program as above[10,11]. A mixture of compounds, including the twenty-seven alkyl halide compounds, were added to raw municipal wastewater to obtain a concentration level of 20 μg/L. Five milliliter aliquots of the aqueous samples were analyzed by purge-and-trap GC/MS using the conditions listed in Table 9. Calibration curves are constructed from the results of purged aqueous solutions. The lower limits of analysis, average recovery and range of relative standard deviation obtained are given in Table 10. These data were collected over a period of two years.

TABLE 8

Analytical Data for Alkyl Halides with Boiling Points less than 150°C

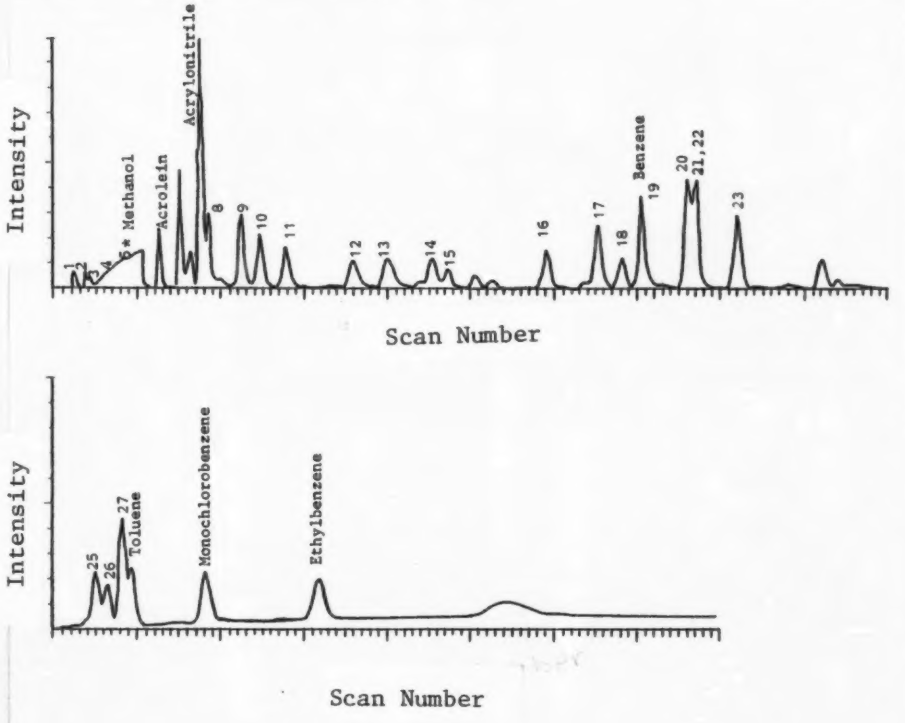
(MEG Category 2A)

MEG Category No.	Compound	Composition	MW	BP (°C)	GC[(a)] Peak No.	RRT[(b)]
1A	Chloromethane	CH_3Cl	50	-24	1	.031
1A	Bromomethane	CH_3Br	94	3	2	.049
1A	Dichlorodifluoromethane	CCl_2F_2	120	-30	3	.054
1A	Vinyl Chloride	C_2H_3Cl	62	-13	4	.056
1A	Chloroethane	C_2H_5Cl	64	12	5	.082
1A	Methylene Chloride	CH_2Cl_2	84	40	6	.156
1A	Trichlorofluoromethane	CCl_3F	137	24	7	.203
1A	1,1 Dichloroethylene	$C_2H_2Cl_2$	96	37	8	.229
1A	Bromochloromethane	CH_2ClBr	129	68	9	.277
1A	1,1 Dichloroethane	$C_2H_4Cl_2$	99	57	10	.304
1B	Trans-1,2-dichloroethylene	$C_2H_4Cl_2$	96	48	11	.340
1A	Chloroform	$CHCl_3$	119	61	12	.440
1A	1,2 Dichloroethane	$C_2H_4Cl_2$	99	84	13	.491
1A	1,1,1 Trichloroethane	$C_2H_3Cl_3$	133	74-76	14	.556
1A	Carbon Tetrachloride	CCl_4	152	77	15	.578
1A	Bromodichloromethane	$CHCl_2Br$	162	89	16	.722
1A	1,1-Dichloropropane	$C_3H_6Cl_2$	113	95-96	17	.796
1B	Trans-1,3-dichloropropylene	$C_3H_4Cl_2$	111	112	18	.830
1B	Trichloroethylene	C_2HCl_3	131	87	19	.861
1B	Cis 1,3-dichloropropylene	$C_3H_4Cl_2$	111	104	20	.925
1A	Dibromochloromethane	$CHClBr_2$	206	118	21	.927
1A	1,1,2-Trichloroethane	$C_2H_3Cl_3$	133	114	22	.927
1A	2-Bromo-1-chloropropane	C_3H_6ClBr	157	120	23	1.00
1A	Bromoform	$CHBr_3$	250	150	24	1.123
1A	1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	168	147	25	1.278
1B	1,1,2,2-Tetrachloroethylene	C_2Cl_4	166	121	26	1.295
1A	1,4-Dichlorobutane	$C_4H_8Cl_2$			27	1.316

(a) GC peak numbers refer to Figure 5.

(b) Relative Retention Times (relative to 2-Bromo-1-chloropropane, RT = 13.72 min.)

Sample:	20 nanograms each Alkyl Halide in 1 μL methane
Column:	0.2% Carbowax 1500, Carbopack C, 80/100 mesh, 2m x 2mm glass
Column Temperature:	25°C $\xrightarrow{\text{rapid}}$ 60°C $\xrightarrow{\text{8°C/min.}}$ 165°C
Carrier Gas:	30 mL/min., Helium
Mass Range:	20-27, 46-260
Integration Time:	1, 2
Seconds Per Scan:	2



(GC peak numbers refer to Table 8)

Figure 5. Total Ion Plot of Alkyl Halides with Boiling Points less than 150°C

TABLE 9

Purge-And-Trap Gas Chromatography Parameters for the Analysis of Alkyl Halides (b.p. < 150°C)

Purge and Trap Unit:	Tekmar LSC-1
Sample Size:	5 mL
Sample Purge Time:	4 minutes
Sample Purge Temperature:	50°C
Trap:	2.67mm I.D.
Trap Packing:	146mm Tenax followed by 54mm Charcoal
Desorb Time:	4 minutes
Desorb Temperature:	180°C
Trap bake out Temperature:	250°C, 10 minutes minimum
GC Column:	Glass, 6 ft. x 2mm I.D., 80/100 Carbopack C/0.2% CW1500
Carrier Gas Flow:	30 mL/min., Helium
GC Program:	20°C to 25°C during sample desorb, rapid heat to 60°C, then 60°C to 165°C at 8°C/min. Hold at 165°C until completion of run.

#7

TABLE 10

Summary of Quality Control Data for Alkyl Halides with Boiling Points less than 150°C

Compound	Lower Limit of Analysis (µg/L)	Average Recovery	Range of Relative Standard Deviations
Chloromethane	5	118	21
Dichlorodifluoromethane	5	194	48
Bromomethane	5	113	22
Vinyl Chloride	5	123	19
Chloroethane	5	108	15
Methylene Chloride	1	138	12-259
Trichlorofluoromethane	1-6	78	11-83
1,1-Dichloroethylene	1-5	72	4-134
1,1-Dichloroethane	1-2	83	2-43
Trans-1,2-dichloroethylene	1	73	3-73
Chloroform	1	82	5-38
1,2-Dichloroethane	1	96	4-35
1,1,1-Trichloroethane	1	82	10-78
Carbon Tetrachloride	1	87	6-44
Bromodichloromethane	1	88	5-24
1,2-Dichloropropane	1	82	3-37
Trans-1,3-dichloropropylene	1	82	4-11
Trichloroethylene	1-2	98	2-78
Cis-1,3-dichloropropylene	1	85	3-20
Dibromochloromethane	1-2	95	4-24
1,1,2-Trichloroethane	1	99	2-13
Bromoform	1-3	74	7-37
1,1,2,2-Tetrachloroethane	1	78	4-75
1,1,2,2-Tetrachloroethylene	1	94	8-79

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B. Species with Boiling Points greater than 150°C

The analytical method originally recommended for alkyl halide compounds (MEG Category 2) with boiling points greater than 150°C in the Level 2 Sampling and Analysis Manual was:

Column: 3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm glass or stainless steel

Example Conditions: Flow Rate: 20 mL/min.

Column Temperature: 100°C isothermal

The analytical finish for this category was evaluated using gas chromatography/electron capture detection (GC/ECD). The instrument used was a Hewlett Packard 5840 Gas Chromatograph. The recommended GC column, 3% SP 2250 on Supelcoport was conditioned overnight at 350°C. A test mixture was prepared, consisting of the compounds in Table 11, in hexane.

The test mixture was chromatographed on the 3% SP 2250 GC column, using the recommended conditions, to determine whether the individual compounds were adequately resolved.

The recommended GC conditions required no modification. A representative gas chromatogram is presented in Figure 6. The appropriate analytical data is given in Table 11.

It was necessary to determine the GC peak retention times of each alkyl halide compound in the test mixture. The retention times were determined by sequentially adding each of the alkyl halide compounds and chromatographing the solution after each addition. The retention times of the alkyl halide GC peaks are given in Table 11. The GC peaks attributable to hexachlorobutadiene and hexachloropropene were not resolved. In GC/MS analysis, appropriate ions could be monitored by mass spectroscopy to distinguish the two compounds.

The lower limit of analysis for each alkyl halide compound was determined. Four test mixtures in hexane, corresponding to 100 pg/µL, 50 pg/µL, 25 pg/µL, and 10 pg/µL of each alkyl halide compound, except hexachlorocyclopentadiene, were prepared. Hexachlorocyclopentadiene was added in the test mixture to give a concentration level ten times the concentration level of the other alkyl halide compounds, namely 1 ng /µL, 500 pg/µL, and 100 pg/µL. These test mixtures were chromatographed using the recommended conditions.

The individual alkyl halide compounds were detected using GC/ECD at 10 picograms injected on the column, except hexachlorocyclopentadiene which was detected at a minimum of 150 picograms injected on the column. Hexachlorocyclopentadiene did not chromatograph well, resulting in GC peak tailing. This tailing resulted in the higher detection limit.

In another program[9], this GC peak tailing was eliminated by programming the column temperature from 40°C (6 minutes) to 140°C at a rate of 4°C/min.

Evidence concerning the precision and accuracy of the GC/MS technique for analyzing alkyl halides is available from other programs[9,10,11]. In one program[11], a mixture of compounds including hexachloroethane, hexachlorobutadiene, and hexachlorocyclopentadiene were added to raw municipal wastewater to give a final concentration of 50 µg/l. One liter aliquots of the aqueous samples were adjusted to a pH greater than 11 with 6N NaOH and extracted three times with methylene chloride (250 mL:100 mL: 100 mL). The sample extracts were dried using Na_2SO_4 and concentrated to 2 mL using Kuderna Danish. The concentrated extracts were analyzed using a 1% SP 2250, 100/120 Supelcoport GC column. The lower limits of analysis, average recoveries and relative standard deviations for the following compounds were obtained over a period of two years.

Compound	Lower Limit of Analysis (µg/L)	Average Recovery	Range of Relative Standard Deviations
Hexachloroethane	10-20	70	26-42
Hexachlorobutadiene	10	57	13-23
Hexachlorocyclopentadiene	-	0	-

Hexachlorocyclopentadiene was not detected using the above procedure. Hexachlorocyclopentadiene is known to be lost during sample preparation as well as during gas chromatography analysis.

In another program[9], a microextraction procedure was used to analyze for the alkyl halides. When this procedure is used, sample preparation is not as extensive as exhaustive extraction procedures described above. The recovery and precision data for hexachlorocyclopentadiene was added to industrial wastewater to give a final concentration level of 42 µg/L. 180 mL aliquots of the aqueous samples, with 60 grams NaCl added, were extracted with 2 mL hexane. This extract was subsequently diluted and analyzed by GC/ECD on a 3% SP 2250, 100/120 Supelcoport GC column. The observed limit of analysis using this technique was 0.02 ng injected on column. The recovery of hexachlorocyclopentadiene from the wastewater was 75% ± 23 (n=10).

TABLE 11

Analytical Data for Alkyl Halides with Boiling Points greater than 150°C

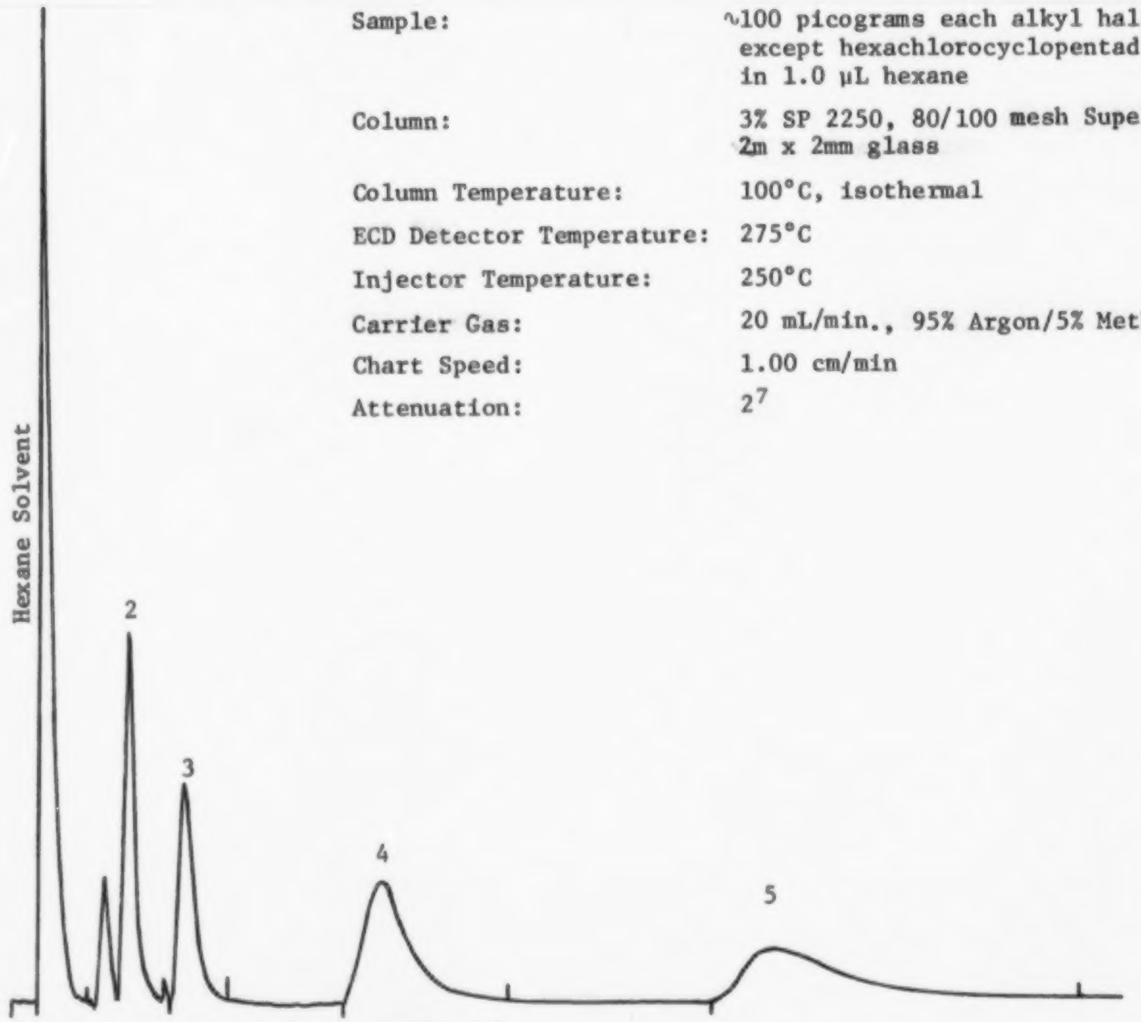
(MEG CATEGORY 2)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC[a] Peak No.	RRt[b]
2A	Tribromomethane	$CHBr_3$	253	150	1	.53
2A	Pentachloroethane	C_2HCl_5	202	162	2	.68
2A	Hexachloroethane	C_2Cl_6	237	186	3	1.00
2B	Hexachlorobutadiene	C_4Cl_6	261	215	4	2.13
2B	Hexachloropropene	C_3Cl_6	249	210	4	2.13
2B	Hexachlorocyclopentadiene	C_5Cl_6	273	240	5	4.52

(a) Numbers refer to Gas Chromatogram, Figure 6.

(b) Relative Retention Times (relative to hexachloroethane, RT = 2.54 min.)

Sample:	~100 picograms each alkyl halide, except hexachlorocyclopentadiene, in 1.0 µL hexane
Column:	3% SP 2250, 80/100 mesh Supelcoport, 2m x 2mm glass
Column Temperature:	100°C, isothermal
ECD Detector Temperature:	275°C
Injector Temperature:	250°C
Carrier Gas:	20 mL/min., 95% Argon/5% Methane
Chart Speed:	1.00 cm/min
Attenuation:	2^7



(GC Peak numbers refer to Table 11)

FIGURE 6. Gas Chromatogram of Alkyl Halides with Boiling Points greater than 150°C.

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Ethers and Halogenated Ethers (MEG Categories 3, 4)

The recommended analytical method for the ether and halogenated ether categories is gas chromatography with flame ionization detection. A specific detector is preferred for the halogenated ethers when concentrations of these compounds are low.

The flame ionization detector is not a selective or specific detector, therefore, care must be taken when identifying GC peaks as ethers or halogenated ethers. The same care should be taken when using halide specific detectors, even though some interferences from non-halogenated constituents are removed. If this category is a major concern, once identities have been assigned using retention time data, gas chromatography/mass spectroscopy (GC/MS) may be used for confirmation. Low ionization voltages using electron impact/mass spectroscopy (EI/MS) or soft ionization techniques, e.g., chemical ionization/mass spectroscopy, may be used in order to obtain molecular ions. This information, combined with EI/MS fragmentation patterns at typical ionization voltages, will be useful when identifying GC peaks.

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ETHERS AND HALOGENATED ETHERS - (MEG CATEGORIES 3, 4)

Recommended Method

Recommended Method: GC/FID

Column: 3% SP 1000 on 100/120 mesh Supelcoport
2m x 2mm glass or stainless steel

Example Conditions: Carrier Gas: 30 mL/min., Helium

Column Temperature: 60°C (2 min.)
↓ 8°C/min.
250°C (Reference 12)

Injector: 250°C

Lower Limit of Analysis: 50 ng Haloethers; 500 ng Ethers

Suggested Alternative Methods

1. Chemical ionization mass spectroscopy can be used for qualitative identification.
2. Haloethers may be determined by GC/MS with a 50 ng detection limit.
3. For haloethers free from interferences:
   - A. The Hall Electroconductivity detector can be used.

Conditions:
Furnace Temperature: 900°C
Transfer Line: 250°C
Hall Electrolyte Flow: 0.3 mL/min., 95% ethanol electrolyte
Hall Electrolyte Makeup: 50 mL/min.$^{-1}$, H_2 reaction gas
Lower Limits of Analysis: .2 pg to 1.1 pg injected of haloethers

(Reference 12)

   - B. The electron capture detector can be used.

4. Alternative GC Columns:

A. The following GC column may be used as a secondary confirmatory GC column when ECD, Hall ECD, or FID is used for detection (dichlorobenzenes frequently interfere with the chromatography of the halogenated ethers).

Column: Tenax GC, 60/80 mesh Supelcoport

Example Conditions: Flow Rate: 40 mL/min.

Column Temperature: 150°C (4 min.)

$\downarrow$ 16°C/min.

310°C

(Reference 12)

B. Suggested for low boiling ethers

Column: 0.1% SP 1000/Carbopack C, 80/100 mesh, 2m x 4mm glass

Example Conditions:	Flow Rate:	65 mL/min.
	Column Temperature:	105°C isothermal
	Injector:	175°C
	FI Detector:	225°C

(Reference 9)

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References

9. Arthur D. Little, Inc., Unpublished Data.

12. Federal Register, Volume 44, No. 233, December 3, 1979, pp. 69517 to 69524.

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ETHERS AND HALOGENATED ETHERS - (MEG CATEGORIES 3, 4)

Method Evaluation

The recommended method for the ether and halogenated ether categories was not specifically evaluated for this program. Data for the recommended methods were available from other sources[9,12].

The 3% SP 1000 GC column (primary recommendation) and Tenax GC columns (Alternative 4A) were recommended for the analysis of priority pollutant halogenated ethers in the Federal Register, Volume 44, No. 233, December 3, 1979[12]. Retention time[12] data, on the two GC columns for the halogenated ethers, using the example GC conditions, are given in Table 12; also included are other appropriate analytical data.

The 0.1% SP 1000, 80/100 Carbopack C GC column (Alternative 4B) was used for the analysis of dioxane and acetone in another program[9]. This GC column is recommended for the analysis of low boiling ethers (b.p. ≤ 100°C). Appropriate analytical data for dioxane are given in Table 12. A representative gas chromatogram is given in Figure 7. As low as 10 ng injeced of dioxane in water was easily detected.

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TABLE 12

Analytical Data for Ethers and Halogenated Ethers

(MEG Categories 3, 4)

MEG Category No.	Compound	Composition	MW	BP (°C)	RRT[a] Column 3% SP1000	RRT[b] Column Tenax GC
3	2-Chloroethylvinyl ether	C_4H_7OCl	107	109	.12	
3	Bis(2-chloroisopropyl)ether	$C_6H_{12}OCl_2$	171		.27	.53
3	Bis(2-chloroethyl)ether	$C_4H_8OCl_2$	143	178	.41	.49
3	Bis(2-chloroethoxy)methane	$C_5H_{10}O_2Cl_2$ 2	173		.58	.54
3	4-Chlorophenyl phenyl ether	$C_{12}H_9OCl$	204	153	.86	.82
3	4-Bromophenyl phenyl ether	$C_{12}H_9OBr$	249	310	.94	.88
					RRT[c]	
4	Dioxane	$C_4H_8O_2$	88	101	3.8 min	

[a] Relative Retention Time (relative to Aldrin, RT=22.6 min.)

[b] Relative Retention Time (relative to Aldrin, RT=18.4 min.)

[c] Refers to Figure 7, GC column: 0.1%SP 1000, Carbopack C, 105°C isothermal.

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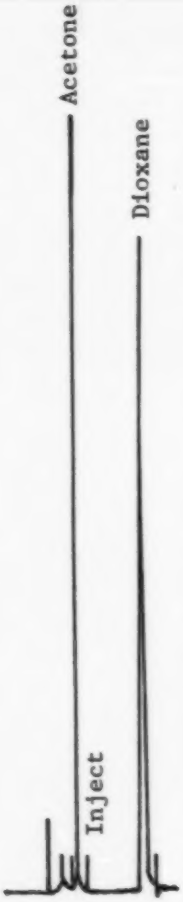

Sample:	2.6 µg Dioxane and .8 µg Acetone in 1 µL H_2O
Column:	0.1% SP 1000/Carbopack C, 80/100 mesh, 1.8m x 2mm
Column Temperature:	105°C (isothermal)
FI Detector:	225°C
Injector Temp.:	175°C
Carrier Gas:	65 mL/min., Helium
Chart Speed:	0.5 cm/min.
Attenuation:	8 x 10^{-10} amp/mV

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Figure 7. Gas Chromatogram of Dioxane (Ethers, Category 3)

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Alcohols (MEG Category 5)

The compounds included in the alcohol category are divided into three subcategories:

Primary Alcohols (5A)
Secondary Alcohols (5B)
Tertiary Alcohols (5C)

The recommended analytical method for this category is gas chromatography with flame ionization detection. GC columns are recommended for two boiling point ranges, less than 200°C and greater than 200°C.

The flame ionization detector is not a selective or a specific detector, therefore, care must be taken when identifying the GC peaks as alcohols during a Level 2 analysis. If this category is a major concern, once identities have been assigned using retention time data from the GC/FID analysis, gas chromatography/mass spectroscopy (GC/MS) may be used for confirmation. Low ionization voltages using electron impact (EI) MS or soft ionization techniques, e.g., chemical ionization mass spectroscopy, may be used in order to obtain molecular ions. This information combined with fragmentation patterns obtained from EI/MS at typical ionization voltages is useful when assigning identities.

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ALCOHOLS - (MEG CATEGORY 5)

Recommended Method

Recommended Method: GC/FID

A. Species with Boiling Points up to 200°C

Column: 0.1% SP 1000 on Carbopack C, 80/100 mesh, 2m x 2mm glass column

Example Conditions: Carrier Gas: 20 mL/min., Helium

Column Temperature: 50°C

↓ 8°C/min.

250°C (hold 5 min.) (Reference 13)

Flame Ionization Detector: 275°C

Injector: 225°C

Lower Limit of Analysis: 10 ng injected

Note the following if organic solvents are used. Toluene must be used as the solvent for alcohol compounds with boiling points up to 150°C. Methylene chloride must be used as the solvent for alcohol compounds with boiling points from 150°C to 200°C.

B. Species with Boiling Points greater than 200°C

Column: 3% SP 2100 on 100/120 mesh Supelcoport, 3m x 2mm glass column

Example Conditions: Carrier Gas: 20 mL/min., Helium

Column Temperature: 100°C (2 min.)

↓ 15°C/min.

250°C (Reference 14)

Flame Ionization Detector: 275°C

Injector: 250°C

Lower Limit of Analysis: 50 ng injected, except α-methylbenzyl alcohol - 100 ng injected

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Suggested Alternative Methods

1. Chemical ionization mass spectroscopy detection is applicable to this category.

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References

13. "Solvent Mixtures and Determination of Water in Solvents," Supelco Bulletin 747C, Supelco, Inc., Bellefonte, PA.

14. Supelco Catalog No. 12, p. 5, Supelco Inc., Bellefonte, PA.

ALCOHOLS - (MEG CATEGORY 5)

Method Evaluation

A. Species with Boiling Points up to 200°C

The analytical method originally recommended for alcohols with boiling points up to 200°C in the Level 2 Sampling and Analysis Manual was:

Column:	0.1% SP 1000 on Carbopack C, 80/100 mesh, 2m x 2mm glass column	
Example Conditions:	Flow Rate:	20 mL/min.
	Column Temperature:	100°C ↓ 8°C/min. 225°C

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph. The recommended GC column, 0.1% SP 1000 on Carbopack C, was conditioned overnight at 225°C. A test mixture was prepared consisting of the compounds listed in Table 13 in methylene chloride.

The test mixture was chromatographed on the 0.1% SP 1000 on Carbopack C using the recommended conditions to determine whether the individual compounds were adequately resolved.

The GC peak attributable to the methylene chloride solvent interfered with the low boiling alcohol compounds. Diethyl ether was substituted as the solvent and the same problem resulted. Toluene was then substituted. The retention time for the toluene GC peak was sufficiently long that the GC peaks attributable to the alcohol compounds with boiling points less than 150°C eluted before the solvent.

The original method recommended that the column be temperature programmed from 100°C to 225°C at 8°C per minute; this was changed to programming from 50°C to 250°C at 8°C per minute. This change was made to resolve the GC peaks of the low boiling alcohols, e.g., methanol and ethanol. A representative gas chromatogram is presented in Figure 8.

The GC peaks attributable to alcohol compounds with boiling points from 150°C to 200°C coeluted with the toluene solvent GC peak. A second test mixture was prepared consisting of the alcohol compounds with boiling points from 150°C to 200°C, Table 13, in methylene chloride. This test mixture was chromatographed using the revised recommended conditions. A representative gas chromatogram is presented in Figure 9.

The choice of solvent, methylene chloride or toluene, is not as important in GC/MS analysis as it is in GC/FID analysis. It is possible in chemical ionization GC/MS that ions unique to the alcohol compounds can be selectively monitored so that the GC peak from the solvent is ignored. GC/FID is essentially a "universal" detector, therefore, the solvent can be a major interference when using GC/FID. In addition, if the concentration of alcohols in an aqueous sample is high (>250 mg/L), the aqueous sample may be injected directly onto the 0.1% SP 1000 GC column. Water is not detected by FID.

It was necessary to determine the GC peak retention times of each alcohol compound in the test mixture. The retention times were determined by sequentially adding each of the alcohol compounds to toluene or methylene chloride, as appropriate, and chromatographing the solution after each addition using the recommended conditions. The GC peak retentions for each of the alcohol compounds in the two test mixtures are presented in Table 13. The order of elution for the isomeric alcohols was 1) tertiary, 2) secondary, and 3) primary alcohols.

The lower limit of analysis for each alcohol compound was determined. Three test mixtures, which consisted of the alcohol compounds with boiling points less than 150°C, were prepared in toluene at concentrations corresponding to 100 ng/μL, 25 ng/μL, and 10 ng/μL for each alcohol. These test mixtures were chromatographed using the revised recommended conditions.

Similarly, three test mixtures consisting of the alcohol compounds with boiling points from 150°C to 200°C were prepared in methylene chloride at concentrations corresponding to 100 ng/μL and 10 ng/μL for each alcohol. These were also chromatographed using the revised recommended conditions.

The individual alcohol compounds were easily detected at 10 nanograms injected on column.

TABLE 13

Analytical Data for Alcohols Test Mixture with Boiling Points up to 200°C

(MEG CATEGORY 5)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC Peak No.	RRT
5A	Methanol	CH_3OH	32	64	$1^{(a)}$	$.14^{(b)}$
5A	Ethanol	C_2H_5OH	46	78	$2^{(a)}$	$.28^{(b)}$
5B	2-Propanol	C_3H_7OH	60	82	$3^{(a)}$	$.57^{(b)}$
5A	1-Propanol	C_3H_7OH	60	97	$4^{(a)}$	$.78^{(b)}$
5C	Tert-Butanol	C_4H_9OH	74	82	$5^{(a)}$	$1.00^{(b)}$
5B	2-Butanol	C_4H_9OH	74	100	$6^{(a)}$	$.157^{(b)}$
5A	1-Butanol	C_4H_9OH	74	118	$7^{(a)}$	$2.0^{(b)}$
5C	2-Methyl-2-butanol	$C_5H_{11}OH$	88	102	$8^{(a)}$	$2.10^{(b)}$
5B	3-Pentanol	$C_5H_{11}OH$	88	116	$9^{(a)}$	$2.67^{(b)}$
5A	Iso-pentanol	$C_5H_{11}OH$	88	132	$10^{(a)}$	$2.90^{(b)}$
5A	Pentanol	$C_5H_{11}OH$	88	138	$11^{(a)}$	$3.28^{(b)}$
5A	n-Hexanol	$C_6H_{13}OH$	102	157	$1^{(c)}$	$.79^{(d)}$
5A	n-Heptanol	$C_7H_{15}OH$	116	176	$2^{(c)}$	$1.00^{(d)}$
5A	n-Octanol	$C_8H_{17}OH$	130	195	$3^{(c)}$	$1.17^{(d)}$

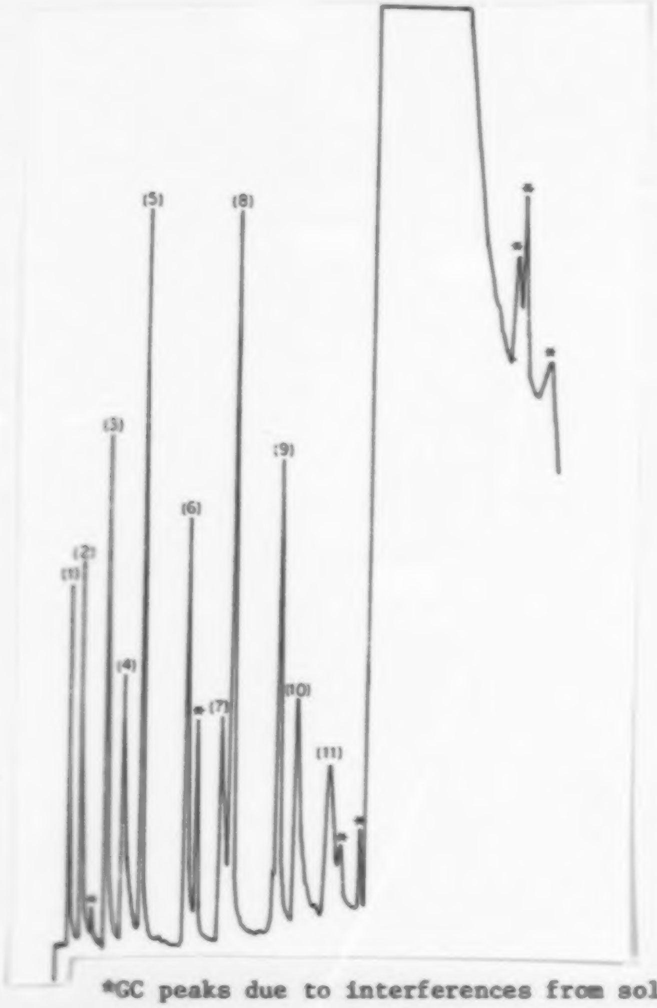
(a) Numbers refer to gas chromatogram, Figure 8.

(b) Relative Retention Times (relative to tert-butanol , RT = 4.5 min.), test mixture is in toluene.

(c) Numbers refer to gas chromatogram, Figure 9.

(d) Relative Retention Times (relative to n-heptanol, RT = 24.4 min.), test mixture in methylene chloride.

Sample:	~100 nanograms of each alcohol compound in 1 μL Toluene
Column:	0.1% SP 1000 on Carbopack C, 80/100 mesh, 2m x 2mm glass
Carrier Gas:	20 mL/min., Helium
Column Temperature:	50°C $\xrightarrow{8°C/min.}$ 230°C
Injector Temperature:	225°C
FI Detector Temperature:	275°C
Attenuation x Range:	1 x 10^{-11} amp/mV
Chart Speed:	0.5 cm/min.



*GC peaks due to interferences from solvent

(GC peak numbers refer to Table 13)

Figure 8. Gas Chromatogram of Alcohol Compounds with Boiling Points up to 200°C

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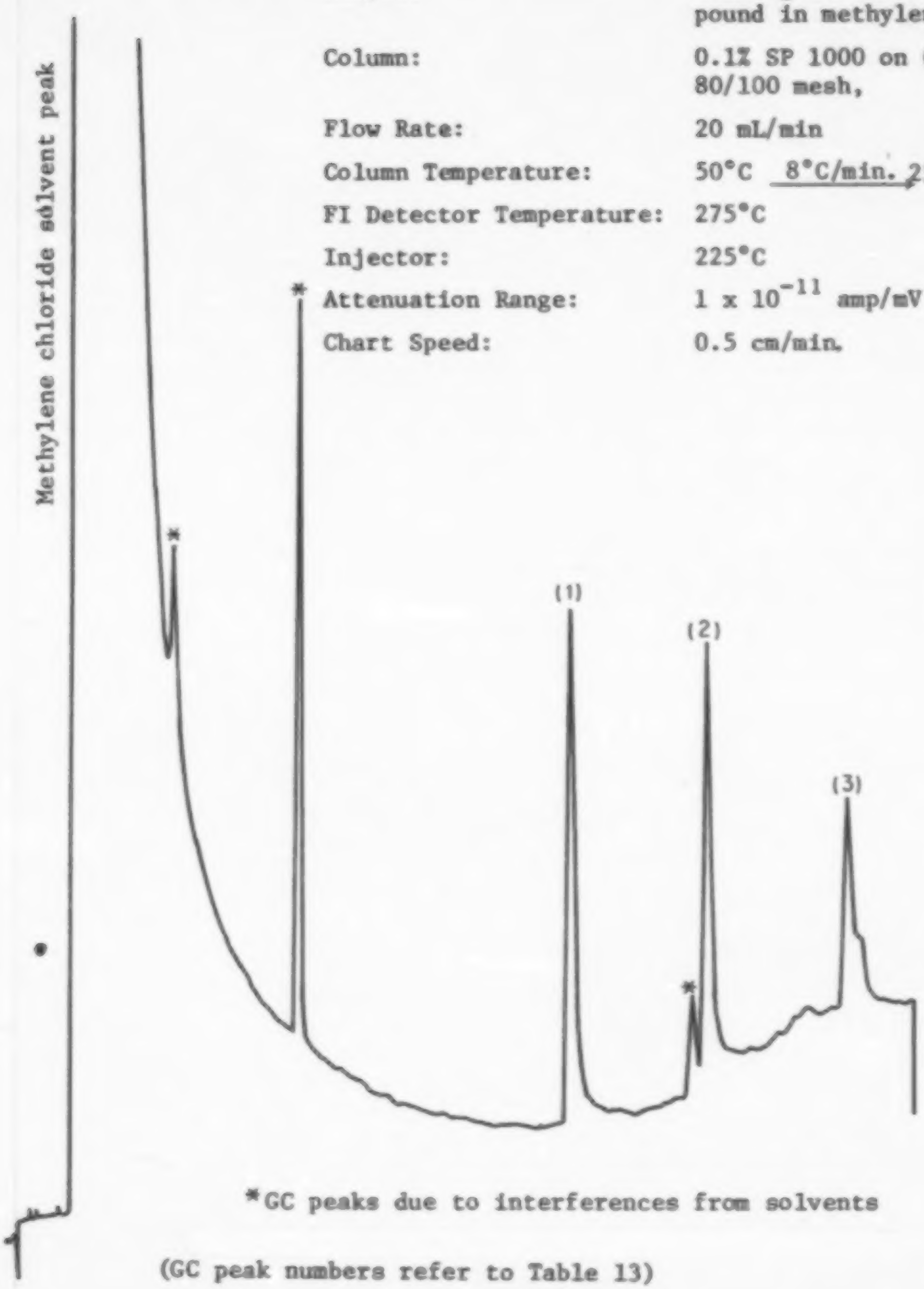

Sample:	∿100 ng of each alcohol compound in methylene chloride
Column:	0.1% SP 1000 on Carbopack C, 80/100 mesh,
Flow Rate:	20 mL/min
Column Temperature:	50°C $\xrightarrow{8^\circ\text{C/min.}}$ 250°C (6 min)
FI Detector Temperature:	275°C
Injector:	225°C
Attenuation Range:	1×10^{-11} amp/mV
Chart Speed:	0.5 cm/min.

*GC peaks due to interferences from solvents

(GC peak numbers refer to Table 13)

FIGURE 9. Gas Chromatogram of Alcohols with Boiling Points up to 200°C

B. Species with Boiling Points greater than 200°C

The analytical method originally recommended for alcohols with boiling points greater than 200°C in the Level 2 Sampling and Analysis Manual was:

Column:	3% SP 2100 on 100/120 mesh Supelcoport, 3m x 2mm glass column
Experimental Conditions:	Carrier Gas: 20 mL/min., Helium
	Column Temperature: 225°C, Isothermal

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization (GC/FID) detection. The instrument used was a Varian 2700 Gas Chromatograph. The recommended GC column, 3% SP 2100 on 100/120 Supelcoport, was conditioned overnight at 350°C.

A test mixture was prepared consisting of the alcohols listed in Table 14 in methylene chloride. This test mixture was chromatographed on the 3% SP 2100 GC column, using the recommended conditions, to determine whether the individual compounds were adequately resolved. The original method recommended a column temperature of 225°C; this was changed to column temperature programming from 100°C (isothermal, 2 min.) to 250°C at 15°C per minute because poor chromatography (peak broadening) was found under the isothermal conditions.

The GC peak retention time of each alcohol compound in the test mixture was determined. The retention times were determined by sequentially adding each of the alcohol compounds to methylene chloride and chromatographing the solution after each addition using the revised recommended conditions. Retention times for each of the alcohol compounds in the test mixture are presented in Table 14. Terpineol and n-decanol were not resolved, however, minor modifications of the GC conditions should suffice if there were a need to analyze the two compounds separately. It is also possible that in chemical ionization GC/MS, ions unique to the alcohol compounds could be monitored so that these two alcohol compounds would be resolved.

The lower limit of analysis for each alcohol compound was determined. Three test mixtures of the alcohol compounds were prepared in methylene chloride solvent at concentration levels corresponding to 500 ng/μL, 300 ng/μL, and 700 ng/μL of each alcohol. These test mixtures were chromatographed using the revised recommended conditions. The individual alcohol compounds, with the exception of α-methylbenzyl alcohol, were easily detected at 170 nanograms injected on column. The GC peak attributable to α-methylbenzyl alcohol showed significant tailing at 170 ng and would be difficult to detect at much lower concentrations. The test mixture was chromatographed on a 1% SP 1240 DA GC column to evaluate whether or not the chromatography and detection limits could be improved. No significant improvements were observed.

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TABLE 14

Analytical Data for Alcohols with Boiling Points greater than 200°C

(MEG Category 5)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC Peak No.[(a)]	RRT[(b)]
5C	α-Methylbenzyl Alcohol	$C_8H_{10}O$	122	205	1	.52
5A	n-Nonanol	$C_9H_{20}O$	144	212	2	.75
5A	n-Decanol	$C_{10}H_{22}O$	158	228	3	.85
5C	Terpineol	$C_{10}H_{17}OH$	154	220	4	.88
5A	n-Undecanol	$C_{11}H_{24}O$	172	243	5	1.00
5A	n-Dodecanol	$C_{12}H_{26}O$	186	255-9	6	1.10

(a) Numbers refer to gas chromatogram, Figure 10.

(b) Relative Retention Times (relative to n-Undecanol, RT = 9.8 min.)

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Sample: 170 nanograms of each alcohol compound in 1 μL methylene chloride

Column: 3% SP 2100 on 100/120 mesh Supelcoport, 3m x 2mm glass

Carrier Gas: 20 mL/min., Helium

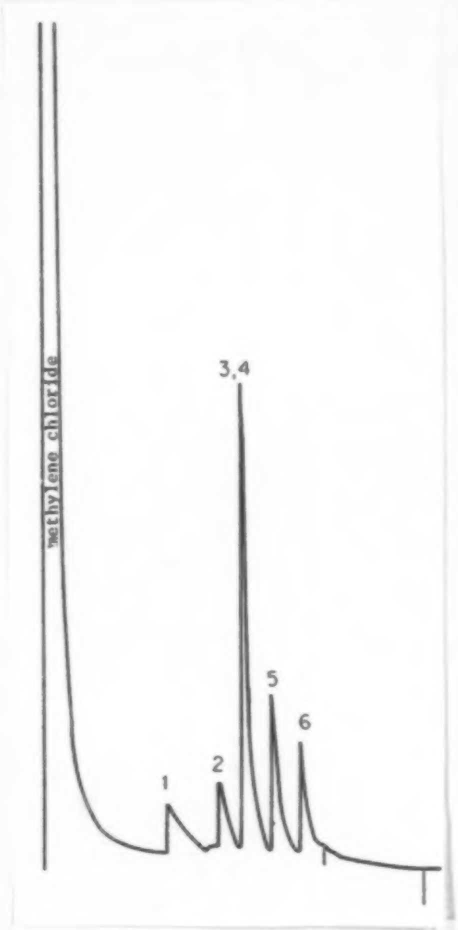
Column Temperature: 100°C (2 min.) $\xrightarrow{15^\circ\text{C/min.}}$ 250°C

Injector Temperature: 250°C

FI Detector Temperature: 275°C

Attenuation x Range: 8×10^{-11} amp/mV

Chart Speed: 0.5 cm/min.



(GC peak numbers refer to Table 14)

Figure 10. Gas Chromatogram of Alcohols with Boiling Points greater than 200°C

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Glycols and Epoxides (MEG Categories 6A, 6B)

The analytical method recommended for glycols is gas chromatography with flame ionization detection (GC/FID). A reverse-phase high performance liquid chromatography procedure is suggested for the epoxides. Epoxides may thermally degrade during GC analysis.

GLYCOLS - (MEG CATEGORY 6A)

Recommended Method

Recommended Method: GC/FID

Column: 3% SP 1000 on 100/120 mesh Supelcoport, 2mm ID x 2m

Example Conditions: Carrier Gas: 20 mL/min. Helium

Column Temperature: 120°C
↓ 1°C/min
140°C

Flame Ionization Detector Temperature: 215°C

Injector Temperature: 215°C

Lower Limit of Analysis: 20 ng to 200 ng injected

Possible Alternative Methods

1. Chemical Ionization Mass Spectroscopy Detection may be applicable to this category.
2. Gas Chromatography on Carbopack C + 0.8% THEED; column 51cm x 2mm ID; Temperature: 115°C, direct aqueous injection. (Reference 15)

Reference

15. DiCorcia, A., Samperi, R., "Gas Chromatographic Determination of Glycols at the Parts-per-Million Level in Water by Graphitized Carbon Black," Anal. Chem., 51(6), 776 (197[illegible]).

EPOXIDES (MEG CATEGORY 6B)

At this time, no satisfactory general method has been found for analysis of this category, although a reverse-phase high performance liquid chromatography (HPLC) technique, using water, acetonitrile, tetrahydrofuran mixtures as the mobile phase, may be suitable for some compounds. (Reference 16)

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Reference

16. Waters Associates, Inc. - personal communication with Lloyd Crossman.

GLYCOLS AND EPOXIDES - (MEG CATEGORIES 6A, 6B)

Method Evaluation

The Level 2 Sampling and Analysis manual suggests that 3% SP 1000 may be a useful stationary phase for gas chromatographic analysis of this category. The analytical finish was evaluated using gas chromatography/flame ionization detection on a Varian 2740 Gas Chromatograph. The column and instrument conditions used are given in the recommendation.

Test mixtures were prepared in water, consisting of the compounds listed in Table 15 and analyzed by direct aqueous injection of 2 μL sample aliquots.

Direct aqueous injection was used because liquid/liquid extraction of glycol compounds into an organic solvent leads to very low recovery efficiencies. Experiments were run to determine the maximum recovery of glycols. One liter sample aliquots containing the glycols listed in Table 16 were extracted with three separate portions of ethyl acetate (250 mL, 100 mL, 100 mL). The recovered organic extracts were concentrated by Kuderna Danish and analyzed by the GC procedure described below. The partition coefficients were calculated using the following relationship:

$$P = \frac{\text{mg in organic phase/volume of organic phase}}{\text{mg in aqueous phase/volume of aqueous phase}}$$

Table 16 lists the data used and the calculated partition coefficients for glycols extracted with ethyl acetate from water. The low glycol extraction efficiency into organic solvents could possible be used to allow removal of extractable interfering components in the sample matrix, e.g., hydrocarbons, aromatics.

Additional experiments were run using the Waters Associates, Inc. Sep-Pack, C_{18} reverse-phase cartridges. The cartridges effectively adsorb a wide variety of organics, but not glycols. Glycols are 100% recovered in the water eluent. The C_{18} Sep-Packs could be used for clean up in the same way that the liquid/liquid extraction above could be used.

Retention times for each of the compounds were determined by sequentially adding each of the glycol compounds to water and chromatographing the mixture after each addition. A representative gas chromatogram is presented in Figure 11.

The lower limits of analysis were 200 ng (equivalent to 100 mg/L water) injected for ethylene glycol, 100 ng (50 mg/L) for 1,3-propane diol, and 20 ng (10 mg/L) injected for both 1,4-butane diol and 1,4-pentane diol.

Two epoxides, propylene oxide and epoxy butane, were also chromatographed

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on the 3% SP 1000 GC column. However, these compounds chromatographed poorly on this column (broad poorly resolved GC peaks). As an alternative to analysis by gas chromatography, a reverse-phase high performance liquid chromatography technique[16] is suggested.

The 3% SP 1000 GC column provides adequate sensitivity and resolution for the analysis of glycols at or below the DMEG values for this category (150 mg/L-water). However, it should be noted that aqueous injections will cause deterioration of this column over time, and the resolution should be monitored to insure adequate performance. As an alternative GC column, the Carbopack C + 0.8% THEED column is recommended. Dicorcia[15] of glycol compounds at mg/L concentration levels.

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TABLE 15

Analytical Data for Glycols

(MEG Category 6A)

Compound	Composition	MW	BP(°C)	GC[(a)] Peak No.	RRT[(b)]
Ethylene glycol	$C_2H_6O_2$	62.07	197	1	0.36
1,3-Propane diol	$C_3H_8O_2$	76.11	213	2	0.67
1,4-Butane diol	$C_4H_{10}O_2$	90.12	230	3	1.00
1,4-Pentane diol	$C_5H_{12}O_2$	104.15	220(713mm)	4	1.14

(a) GC peak numbers refer to Figure 11.

(b) Relative retention times (relative to 1,4-butane diol, RT = 13m).

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Sample: 2 µg each glycol compound in 2 µL water

Column: 3% SP 1000, 100/120 mesh Supelcoport
2m x 2mm ID glass

Carrier Gas: 20 mL/min, Helium

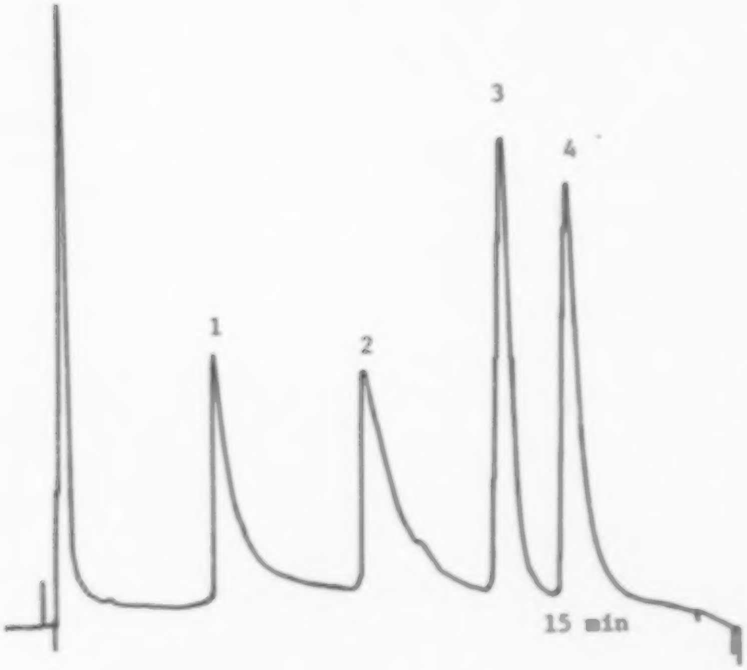
Column Temperature $120^\circ\mathrm{C} \xrightarrow{1^\circ\mathrm{C/min}} 140^\circ\mathrm{C}$

Injector Temperature: 215°C

FI Detector Temperature: 215°C

Attenuation Range: 8 x 10^{-11} amp/mV

Chart Speed: 0.5 cm/min.



(GC peak numbers refer to Table 15)

Figure 11. Gas Chromatogram of Glycols

TABLE 16

Partition Coefficients Calculated for Glycols
(MEG Category 6A)

Compound	mg Added to Aqueous Sample	mg Recovered	Volume Recovered (mL) Organic	Percent Recovery	Log P*
1,3-Propane diol	1077	1.23	160	.114	-2.14
	1077	3.72	100	.346	-1.46
	1077	3.39	100	.315	-1.50
1,4-Butane diol	697.8	6.19	160	.887	-1.25
	697.8	5.51	100	.791	-1.10
	697.8	5.45	100	.781	-1.11
	697.8	7.95	160	1.14	-1.14
	697.8	2.67	100	.383	-1.41
	697.8	5.07	100	.727	-1.14
1,4-Pentane diol	553.9	2.68	160	.48	-1.52
	553.9	3.59	100	.65	-1.19
	553.9	3.44	100	.62	-1.21
	553.9	3.91	160	.71	-1.35
	553.9	1.47	100	.27	-1.57
	553.9	2.884	100	.52	-1.28

* Aqueous phase contains 9% ethyl acetate (V/V)

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Aldehydes and Ketones (MEG Categories 7A, 7B)

The compounds in the aldehyde category (MEG Category 7A) include both aliphatic and aromatic aldehydes. The recommended method for this category is a 2,4-dinitrophenyl hydrazone-high performance liquid chromatography (DNPH-HPLC) method.

The compounds in the ketone category (MEG Category 7B) also includes aliphatic and aromatic species. The recommended analytical method for ketones is gas chromatography/mass spectroscopy. There is evidence that the DNPH-HPLC procedure for aldehydes will work for the ketones. However, GC/MS is the more powerful technique for identifying specific compounds.

ALDEHYDES AND KETONES (MEG CATEGORIES 7A, 7B)

Recommended Method

7A. Aldehydes

Column: Zorbax ODS, 5 micron, DuPont
2.5cm x 4.6mm ID stainless steel

Mobile Phase: Acetonitrile/Water, Flow Rate: 1.5 mL/min. (Reference 17)

Detector: UV, λ 254

DNPA Derivatization: React with 2,4-dinitrophenylhydrazine in 2 N HCL. Extract aqueous sample with chloroform. Wash extract with 2 N HCL and then with distilled H_2O, concentrate extract to dryness. Dissolve dried sample in acetonitrile. (Reference 18)

Lower Limits of Analysis: 0.1 ng to 0.5 ng injected

This procedure is also applicable for ketones (MEG Category 7B).

7B. Ketones

Recommended Method: GC/MS

Column: 0.1% SP 1000 on 80/100 mesh Carbopack C
2 mm x 3 m glass column

Example Conditions: Carrier Gas: 20 mL/min. Helium

Column Temperature: 60°C

$$60^\circ C \xrightarrow{5^\circ C/min} 210^\circ C \ (10\ min.)$$

Injector Temperature: 230°C

Lower Limit of Analysis: 10 ng injected

Suggested Alternative Methods

1. For Ketones - GC/FID (same chromatographic conditions as above) is an alternative detection system for preliminary evaluation or for interference-free samples.

   Flame Ionization Detector Temperature: 250°C
   Lower Limit of Analysis: 5 ng injected

2. For Ketones - An alternative column is 60/80 Carbopack C, 0.2% Carbowax 1500, 2m x 2mm glass column. (Reference 19)

3. For Aldehydes - An alternative method for this category is the 3-methyl-2-benzothiazolone (MBTH) method for total aliphatic aldehydes (Reference 20). For air samples, the air is bubbled through an aqueous solution of .05% MBTH. For aqueous samples, an aqueous solution of MBTH is added to the sample aliquot to give a final concentration of 0.05% MBTH. After one hour, 2 mL of an oxidizing reagent, 1.0% ferric chloride and 1.6% sulfamic acid, is added to a 10 mL aliquot of the MBTH solution. The absorbance of the solution is read at 628 nm.

   When the composition of aldehydes in a sample is unknown, a formaldehyde calibration curve is recommended for quantification and the aldehydes reported as formaldehydes. A correction factor may be used to report the aldehydes as butyraldehyde. (Reference 21,22)

   The detection limit in air is approximately 1-10 ppm and in water is approximately 30 ppb for formaldehyde and 75 ppb for butyraldehyde.

References

17. Unpublished data, Arthur D. Little, Inc.

18. Kuwata, K., M. Verbori and Y. Yamasaki, "Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs and their 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography," Journal of Chromatographic Science, 17, 264, May 1979.

19. Supelco Catalog No. 14, p. 36.

20. Hauser, Thomas, R. and Rodney L. Cummins, "Increasing Sensitivity of 3-Methyl-2-Benzothiazolone Hydrazone Test for Analyses of Aliphatic Aldehydes in Air," Anal. Chem., 56, 679 (1964).

21. Altshuller, A. P., Leng, L. G., Anal. Chem., 35, 1541 (1963).

22. Altshuller, A. P., McPherson, S. P., Air Pollution Control Assoc., 13, 109 (1963).

ALDEHYDES AND KETONES (MEG CATEGORIES 7A, 7B)

Method Evaluation

Aldehydes (MEG Category 7A)

The analytical method originally recommended for aldehydes (MEG Category 7A) in the Level 2 Sampling and Analysis manual is the 5-methyl-2-benzothiazolone hydrazone (MBTH) method for total aldehydes, as modified by Hauser[20]. This colorimetric technique, rather than a gas chromatographic technique, was recommended because aldehydes are known to oxidize in the presence of air. It was anticipated that these reactive species would best be sampled by collection in an aqueous medium and, therefore, that an analysis method directly applicable to aqueous samples was preferable to a GC approach.

In the MBTH procedure, total aliphatic aldehydes are treated with MBTH in the presence of ferric chloride to form a blue cationic dye in acidic solution. Hauser modified the basic procedure by adding sulfamic acid during the oxidizing step of the reaction, which eliminated turbidity in the solution. Previous workers had overcome turbidity in the solution by diluting with acetone, which subsequently reduced the potential sensitivity of the MBTH procedure. Hauser observed that the sensitivity of the method was increased approximately sixfold when sulfamic acid was used, rather than diluting with acetone.

The total aldehyde MBTH procedure was evaluated by determining the linear (Beer's Law) range for two specific aldehyde-MBTH complexes. Beer's Law is represented by the formula

$A = \varepsilon bc$, where A is the absorbance,
ε is the molar absorptivity,
b is the length of the light path and
c is the molar concentration.

It was also determined whether the absorbances for two different aldehydes in a solution were additive. The instrument used for all quantitative colorimetric determinations was a Perkin-Elmer Coleman 55 spectrophotometer with a 1 cm cell path length.

Five test solutions and a reagent blank of formaldehyde were prepared in distilled, deionized, organic-free water and added to a 0.05% MBTH solution. The μMolar concentration values of formaldehyde in the final MBTH solution corresponded to the levels listed in Table 17. These solutions were analyzed using the method detailed. The absorbances read at 628 nm are presented in Table 17, and the corresponding calibration curve is presented in Figure 12. The slope of the formaldehyde curve is .0474, therefore, the molar absorptivity ($a = A/bc$) of the formaldehyde complex at 628 nm is 47,400 absorbance units·liters/cm·moles. The curve is linear for formaldehyde concentrations of .034 μM to 16.7 μM.

Five test solutions of butyraldehyde and a reagent blank were also prepared and added to a 0.05% MBTH solution. The μMolar concentration values of butyraldehyde in the MBTH solution corresponded to the levels listed in Table 17. These solutions were analyzed using the revised recommendation. The absorbances read at 628 nm are presented in Table 17, and the corresponding calibration curve is presented in Figure 12. The molar absorptivity of butyraldehyde is 36,800. The curve is linear for butyraldehyde concentrations from .014 μM to 6.94 μM.

The molar absorptivity for formaldehyde (47,400) is higher than that for butyraldehyde (36,800). This difference can be accounted for when the composition of aldehydes in a sample is unknown and a formaldehyde calibration curve is used for quantification. Altshuller[21,22] used the MBTH procedure (without the addition of sulfamic acid) for the analysis of aldehydes in auto exhaust polluted atmosphere. We used a multiplication factor of 1.25 ± 0.10 to convert aldehydes measured as formaldehydes to total aliphatic aldehydes. This multiplication factor is apparently consistent with the data presented for aldehydes in this report, i.e., the ratio of the slopes for formaldehyde (.0474)/butyraldehyde (.0368) is 1.29. Therefore, total aldehydes could be reported as butyraldehyde, rather than formaldehyde, by using a multiplication factor.

Formaldehyde and butyraldehyde were analyzed together to determine if the absorbances measured for the two compounds were additive. The calculated absorbance value was determined by adding together the absorbance values measured previously for each aldehyde compound. The calculated and measured absorbance values are presented below:

Formaldehyde Concentration, μM	Butyraldehyde Concentration, μM	Calculated Absorbance	Measured Absorbance
3.33	1.39	.214	.211

The agreement between the calculated and measured results are quite good, i.e., within 6%, which is within the estimated precision (5%) of the absorbance determination with the instrumental system used.

The detection limit for formaldehyde and butyraldehyde is approximated from the calibration curves (Figure 12) at .50 μM in 50 mL of MBTH solution, which is equivalent to .75 μg/50 mL of formaldehyde and 1.8 μg/50 mL of butyraldehyde. The aqueous sample aliquot added to MBTH solution was 25 mL, therefore, the detection limit for the original sample was 1.8 μg/25 mL or 72 μg/L of butyraldehyde and .75 μg/25 mL or 30 μg/L of formaldehyde. The detection limit could be improved by adding smaller volumes of the MBTH solution at higher concentration levels. (For example, 5 mL of a 0.5% MBTH solution could be added to a 45 mL sample aliquot containing 1.8 μg of butyraldehyde, so that the final concentration of the MBTH solution was still 0.05% and the butyraldehyde concentration would be equivalent to 40 μg/L).

TABLE 17

Analytical Data For Aldehydes

(MEG Category 7A)

MEG Category No.	Compound	Composition	MW	BP, °C	µM	Absorbance,* 628 nm
7A	Formaldehyde	CH_2O	30	-21	.034	-
					.334	.010
					1.67	.069
					3.33	.153
					16.7	.786
7A	Butyraldehyde	C_4H_8O	72	75	.014	.004
					.139	.011
					.694	.032
					.139	.058
					6.94	.261

* Estimated precision of Absorbance determination with the instrumental system used is on the order of 5%. Additional uncertainty may be associated with the variability in color forming reaction process.

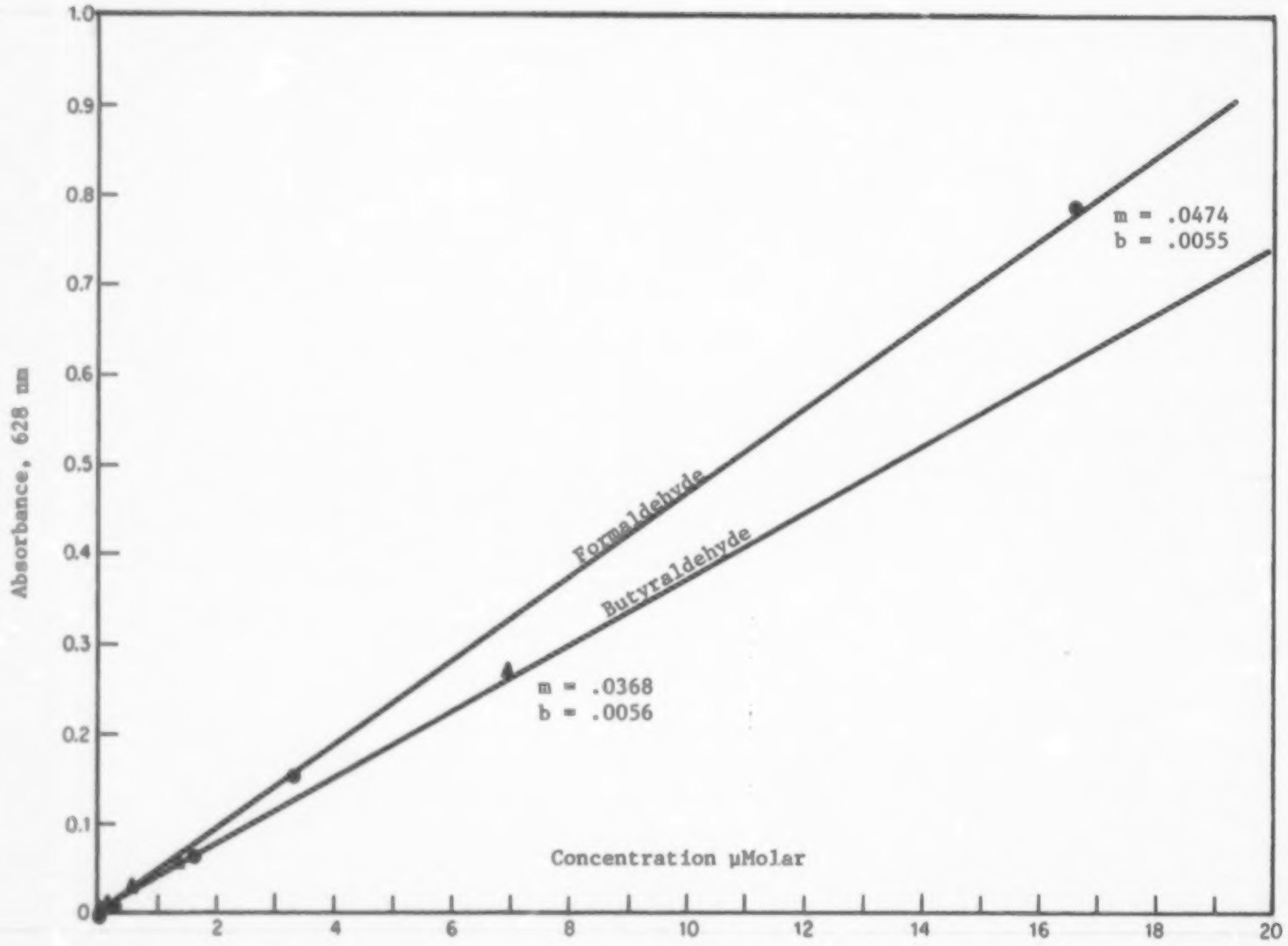


Figure 12. Calibration Curves for Formaldehyde and Butyraldehyde

Ketones (MEG Category 7B)

The analytical method originally recommended for ketones (MEG Category 7B) in the Level 2 Sampling and Analysis manual is:

Column: 3% SP 2250 on 100/120 Supelcoport
2m x 2mm glass

Conditions: Carrier Gas: 20 mL/min

Column Temperature: 60°C
↓ 6°C/min
200°C

Detection Limit: 50 ng injected

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph. The recommended column, 3% SP 2250 on 100/120 Supelcoport, was conditioned overnight at 300°C.

A test mixture was prepared consisting of the ketones listed in Table 18 in methylene chloride. This mixture was chromatographed on the 3% SP 2250 GC column using the recommended conditions. The original method recommended GC column temperature programming from 60°C to 200°C at 6°C per minute; this was changed to column temperature programming from 60°C, isothermal 4 minutes to 250°C, isothermal 4 minutes, at 10°C per minute. This change was made to reduce the peak broadening and tailing observed using the original conditions, to resolve the low boiling ketones, e.g., 2-butanone (b.p. 80°C), from the solvent GC peak, and to elute the high boiling ketones, e.g., 2-nonanone (b.p. 195°C), from the column. The modified GC column temperature programming did improve the chromatography of the ketone GC peaks somewhat. However, unacceptable ketone GC peak broadening and tailing were still observed. Therefore, an alternative GC column was evaluated.

The alternative GC column, 0.1% SP 1000 on 80/100 Carbopack C, was conditioned overnight at 180°C. The instrument used was a Hewlett Packard 5840A Gas Chromatograph with a flame ionization detector. The test mixture (Table 18) was chromatographed on the 0.1% SP 1000, 80/100 Carbopack GC column using the following conditions:

Carrier Gas: 20 mL/min Helium

Column Temperature: 50°C (2 min) $\xrightarrow{5^\circ\text{C/min}}$ 210°C (10 min)

It was necessary to use sample injection volumes ≤0.5 µL to avoid plugging of the 0.1% SP 1000 Carbopack C column.

GC peak retention times for each of the ketones in the test mixture were determined. The retention times were determined by sequentially adding each of the ketones to methylene chloride and chromatographing the solution after each addition using the conditions above. Acetone could not be resolved from the GC solvent peak, even at initial temperatures close to ambient temperature (35°C). Since acetone could not be resolved satisfactorily, the temperature program was changed to 60°C $\xrightarrow{5^\circ C/min}$ 210°C (10 min), to reduce the analysis time. If it is necessary to analyze for acetone, a different GC column, such as 60/80 Carbopack C/0.2% Carbowax 1000 would be needed. Retention times for each compound in the test mixture using these revised GC conditions are presented in Table 18. 2-Pentanone and 3-pentanone could not be resolved and isomers such as these would probably have to be analyzed as a pair. A representative gas chromatogram is given in Figure 13.

The lower limit of analysis for each ketone was determined. A test mixture of the ketones was prepared in methylene chloride to give a concentration level of 10 ng/μL. The individual ketones were easily detected at 5 ng injected on column.

If concentration levels greater than 250 ng injected on column need to be analyzed, it will probably be necessary to use a 3% SP 2250 GC column. The 0.1% SP 1000 Carbopack C GC column will plug with high levels of material injected on the column.

TABLE 18

Analytical Data for Ketones

(MEG Category 7B)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC Peak No.[a]	RRT[b]
7B	Acetone	C_3H_6O	58	56	-	-
7B	2-butanone	C_4H_8O	72	80	1	.26
7B	2-pentanone	$C_5H_{10}O$	86	102	2	.54
7B	3-pentanone	$C_5H_{10}O$	86	102	2	.54
7B	2-methylcyclohexanone	$C_7H_{12}O$	112	165	3	1.00
7B	4-methyl-3-penten-2-one (mesityl oxide)	$C_6H_{10}O$	98	130	4	1.03
7B	3-methylcyclohexanone	$C_7H_{12}O$	112	169	5	1.05
7B	2-nonanone	$C_9H_{18}O$	142	195	6	2.01

(a) Numbers refer to gas chromatogram, Figure 13

(b) Relative retention times (relative to 2-methylcyclohexanone, RT = 25.98 min)

Sample: 100 ng of each ketone compound in 0.5 μL methylene chloride

Column: 0.1% SP 1000 on 80/100 Carbopak C, 3m x 2mm glass

Carrier Gas: 20 mL/min., Helium

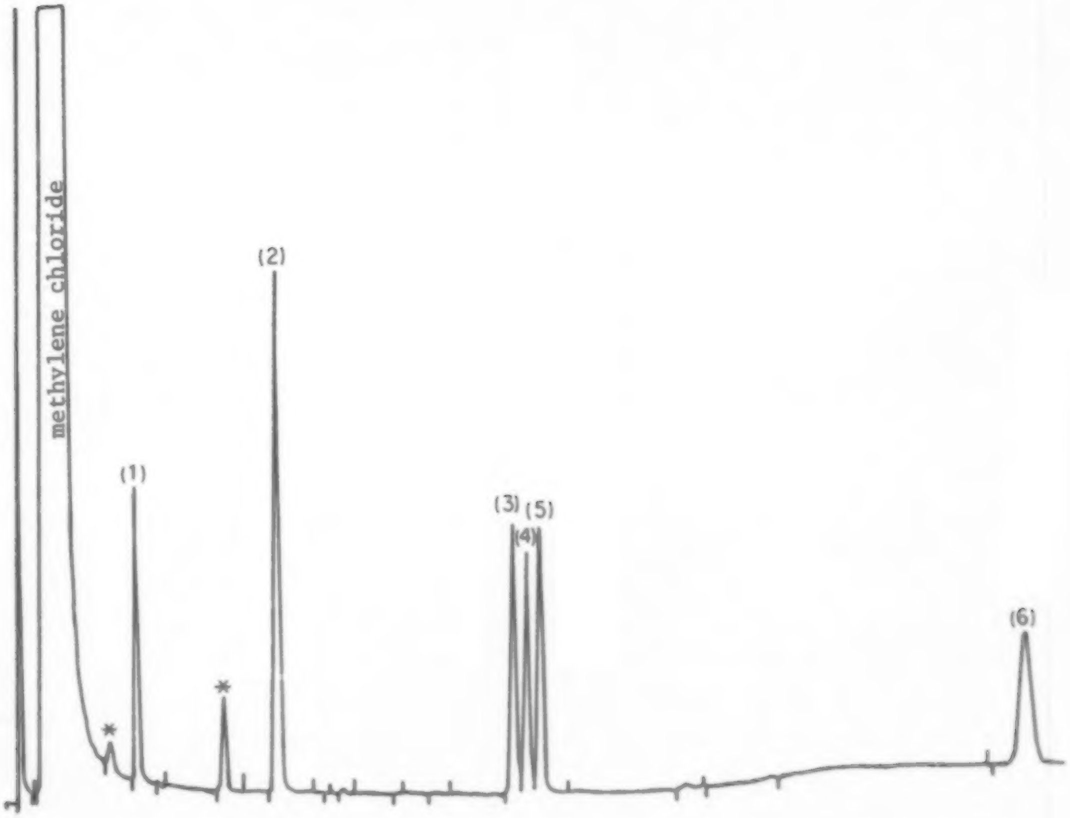
Column Temperature: 60°C $\xrightarrow{5^\circ/\text{min}}$ 210°C (10 min)

Injector Temperature: 230°C

FI Detector Temperature: 275°C

Attenuation: 2^7

Chart Speed: 0.5 cm/min.



*GC peaks attributable to the methylene chloride solvent

(GC peak numbers refer to Table 18)

Figure 13. Gas Chromatogram of Ketones

High Performance Liquid Chromatography Method for Aldehydes (MEG Category 7A)

The recommended method for aldehydes (MEG Category 7A) is a high performance liquid chromatography procedure, as described by Kuwata.[18] Using this procedure, aliphatic and aromatic aldehydes are analyzed as 2,4-dinitrophenyl hydrazone (DNPH) derivatives on a reverse-phase HPLC column. Similar to the colorimetric procedure described previously, this method is designed to prevent aldehyde losses due to oxidation in air. Air samples are collected in an aqueous medium and subsequently derivatized for HPLC analysis. The derivatization procedure is described in the recommended method. Kuwata[18] reported that aliphatic and aromatic aldehydes may be detected at levels between 0.1 ng and 0.5 ng for each free aldehyde on column. A mixture of thirteen aliphatic and aromatic aldehydes were recovered from air sample spikes at 96% ± 5.5. Ketones may also be analyzed using this procedure. Ketones of similar molecular weight to the aldehydes were adequately resolved in this work.

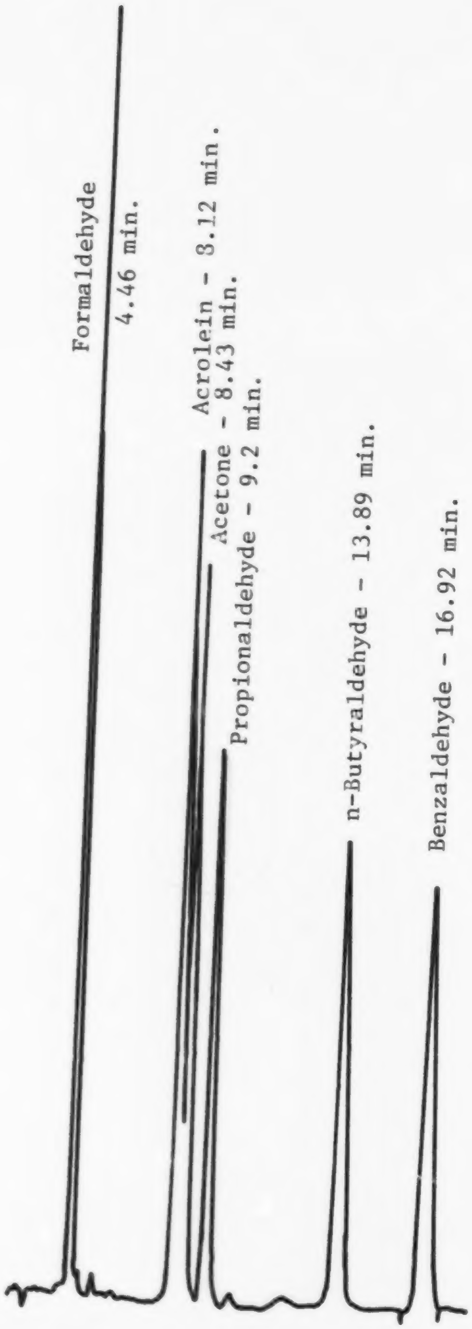
This procedure was evaluated during another program.[9] A representative HPLC chromatogram is presented in Figure 14 and appropriate analytical data is presented in Table 19. In this work, the HPLC column used was a 5 micron Zorbax (DuPont) reverse-phase column.

TABLE 19

Analytical Data for Aldehydes and Ketones

(MEG Categories 7A and 7B)

MEG Category No.	Compound	Formula	MW	BP, °C	Retention Time of DNPH Derivative
7A	Formaldehyde	CH_2O	30	-19.5	4.46 min
7A	Acrolein	CH_2=CHCHO	56	52.5	8.12 min
7B	Acetone	C_3H_6O	58	56.5	8.43 min
7A	Propionaldehyde	C_3H_6O	58	49	9.2 min
7A	n-Butyraldehyde	C_4H_8O	72	74.8	13.89 min
7A	Benzaldehyde	C_7H_6O	106	179	16.92 min



Sample:	32 ng each compound in 20 μL acetonitrile
Column:	Zorbax ODS, 5 micron - DuPont, 4.6mm x 25cm
Mobile Phase:	62% acetonitrile/38% water
Flow Rate:	1.5 mL/min.
Detector:	UV - λ254, Range - x.01
Recorder:	x10 mV

Figure 14. HPLC Chromatogram of DNPH Derivatives of Aldehydes and Ketones

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Carboxylic Acids (MEG Categories 8A, 8B)

The compounds included in the carboxylic acid category include mono- and dicarboxylic acids, as well as carboxylic acids with additional functional groups.

The recommended analytical finish for monocarboxylic acids (to C5) is gas chromatography/mass spectrometry. The recommended analytical method for dicarboxylic acids, aromatic and aliphatic (>C5) acids and acids with additional functional groups is reverse-phase high performance liquid chromatography. Ion chromatography is also recommended as an alternative procedure.

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CARBOXYLIC ACIDS - (MEG CATEGORIES 8A, 8B)

Recommended Method

A. Formic, Acetic Acids, Mono-Acids to C5

Recommended Method: GC/MS

Column:	Carbopack B, 3% Carbowax 20 M, 0.5% H_3PO_4, 76cm x 4mm ID glass column
Example Conditions:	Flow Rate: 60 mL/min. Column Temperature: 160°C, isothermal
Detection Limit:	50 ng injected

Expected Retention Times (Reference 23)

formic	<1	min.
acetic	1	min.
propionic	1.6	min.
isobutyric	3.6	min.
n-butyric	5	min.
n-valeric	15	min.

B. Dicarboxylic Acids, Aromatic Acids, Aliphatic Acids >C5, and Acids with Additional Functional Groups

Recommended Method: Reverse Phase HPLC

Column:	MicroPak-CH (octadecylsilane), μBondapak/C18, 30cm x 4mm ID, or equivalent
Mobile Phase:	Water, acidified to pH 2.5 with $HClO_4$ and operated at 60°C for MicroPak-CH; water methanol mixtures for μBondapak C18; ∿2 mL/min.
Detector:	UV, (variable wavelengths) at 210 nm for aliphatic acids, and 254 nm for others
Detection Limit:	1-100 μg/mL, (50 μL injected)

Suggested Alternative Methods

1. For samples in which known interferences are absent, determination of acids as methyl or methylsilyl esters with detection by GC/FID.

2. Ion-exchange liquid chromatography, using either:

   a. Cation-exchange resins (Dowex 50W-X4 or Aminex 50W-4X) with 0.001N or 0.01N HCl eluent, or;

   b. Strongly basic anion-exchange resins (e.g., Dowex 1-X8), with 0.2M NaOAc and HOAc as eluents. Detection by RI or UV at 210 nm or 254 nm as appropriate, or electro conductivity detector (Reference 24).

3. Ion Chromatography Exclusion - <C5 low molecular weight mono- and dicarboxylic acids,

   250 mm Dionex Exclusion
   500 mm Dionex Halide Suppressor (Ag^+ form) with .001 M HCl eluent
   (Reference 25)

References

23. Supelco Catalog No. 13, p. 3, Supelco, Inc., Bellefonte, PA.

24. Richards, M., "Separation of Mono- and Dicarboxylic Acids by Liquid Chromatography," Journal of Chromatography, 115, 259 (1975).

25. Menzies, K.T. and I. Bodek, "Ion Chromatographic Analysis of Organic Acids in Diesel Exhaust and Mine Air," paper presented at Second Chemical Congress of the North American Continent, Las Vegas, Nevada, August 1980.

CARBOXYLIC ACIDS - (MEG CATEGORIES 8A, 8B)

Method Evaluation Data

The analytical method which has been evaluated for analysis of dicarboxylic acids is ion chromatography, because it offers several advantages over other reported methods. Analysis using ion chromatography requires no extraction of the samples from aqueous media; extraction of these acids from water into an organic solvent is difficult due to their extreme preference for the aqueous media. Ion chromatography analysis does not require derivatization of the acids, and detection of low concentration levels of acids is possible using the conductivity detector. Interference from non-ionized species in the sample matrix is minimized both by the chromatography and by the lack of detection by the conductivity detector.

The analytical method was evaluated using a Dionex Model 14 Ion chromatograph. Two 3 x 500mm anion separator columns (Dionex) equipped with a 0.008 M Na_2CO_3 in 25% aqueous methanol was used at a flow rate of 1.45 mL/min. The columns were adjusted to the highly non-aqueous eluent by increasing the methanol content of the eluent by steps of 5% over a period of one hour.

Test mixtures were prepared of the dicarboxylic acids listed in Table 20 in distilled water, using standards obtained from Polyscience Corporation. A 100 µL sample injection loop was used for sample introduction. Retention time determination and assignment of chromatographic peaks to the individual acids were made by sequentially adding each of the acids to water and chromatographing the mixture after each addition.

Retention times for each of the acids in the mixture are presented in Table 20. Using the described chromatographic conditions, glutaric, adipic, and pimelic acids were not resolved from each other, nor were malonic and suberic resolved. The ion character of these higher chain acids is apparently too similar, as suggested by their pK_a values (Table 20), to allow great differences in interaction with the ion exchange column.

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The detection limit for each acid was estimated using a required detector response of 0.005 µMhos. Nearly all of the acids can be analyzed at 1 ppm or lower concentrations. This lower limit of analysis is adequate as illustrated by the MATE value in water of one of the acids (maleic) of 15 ppm. A sample chromatogram of four of the acids at ppm concentrations is given in Figure 15. The lack of resolution of some of the acids is illustrated in Figure 16.

Linear response is observed over the concentration range of 1 to 10 ppm in the sample for these acids as illustrated in Figure 17.

To determine the extent of interference of common inorganic ions in the analysis for the dicarboxylic acids, retention times for fluoride, chloride, nitrate, and sulfate were determined using the same chromatographic conditions. Fluoride and chloride elute early in the chromatogram

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(retention times of 6.9 and 10.1 minutes, respectively), and thus do not interfere. However, great interference is observed from nitrate (retention time, 23.8 minutes) in the analysis of maleic acid, and by sulfate (retention time, 37.8 minutes) in the analysis of oxalate.

In summary, although the ion chromatographic (anion exchange) method is sensitive and is capable of analyzing these acids, it is subject to interferences and to incomplete resolution of some of the acids. Further investigations into the use of different columns and eluents, such as sodium borate, might overcome some of these difficulties. A possible modification of this procedure includes the use of a newly introduced column by Dionex which uses an ion chromatography exclusion technique. This column does not retain ionized species (i.e., strong inorganic acids and their salts), and thus organic acids which are weakly dissociated may be separated from these ions. The organic acids are separated in a very low conductance background, thus extending detection limits to less than 1 ppm.

This ion chromatography exclusion method which has previously been utilized for separation of strong acids as a group from weak acids[26], and individual Krebs Cycle Acids[27] was evaluated for analysis of low molecular weight (<C5) monocarboxylic acids in a dilute diesel exhaust and mine air matrix[25]. The analytical method was evaluated using a Dionex Model 14 Ion Chromatograph and the following conditions:

Ion Chromatographic Exclusion (ICE) Conditions

Instrument	Dionex Model 14 Ion Chromatograph
Eluent	0.0001 M HCL
Flow Rate	0.7 mL/min.
Detector	Conductivity
Sensitivity	3 μmhos full scale
ICE Columns	9 x 250 mm Dionex Exclusion 3 x 500 mm Dionex Halide Suppressor (Ag^+ Form)
Sample Volume	100 μL, Waters Associates Autoinjector (Model 710 A)
Recorder	HP 7133A
Chart Speed	0.5 cm/min.

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The concentration of the acid eluent (0.0001 M HCl) was optimized for this specific analysis but concentrations in the range of 0.01 M to 0.001 M may be suitable for similar analyses. The weakly acidic nature of the eluent influences the ionization of each carboxylic acid in proportion to its pK and thus its retention time.

Standard acid mixtures were prepared from sodium salts for assignment of chromatographic peaks to individual acids and determination of retention times. A typical ion chromatogram of formic and sulfuric acid is shown in Figure 18. The retention time for sulfuric and formic acid is 9.8 and 15.4 minutes, respectively. The peak height is linear with formic acid concentration over the range of 0.3 to 10 µg/mL. The corresponding linear range for acetic acid is 3 to 100 µg/mL (Figure 19).

The precision of the ICE method was determined by analyzing six replicates of two standard solutions containing strong acids (i.e., H_2SO_4) and formic acid, acetic acid and carbonic acid. Carbonic acid is present as a result of the use of Na_2CO_3 in the standard solution matrix and dissolution of atmospheric carbon dioxide. At formic acid concentrations of 5.0 and 10 mg/L, the measured mean concentrations were 5.08 and 10.0 mg/L, respectively. The relative standard deviation (CV) was 0.025 and 0.016, respectively.

The accuracy of the ICE method was assessed by using the standard addition technique. Four mine samples containing measured concentrations of formic acid of about 0.8 to 1.1 µg/mL were spiked with a known volume of formic acid standard solution sufficient to double the sample concentration. The observed concentration indicated agreement of better than ±12% with an average agreement within ±5%.

Standard Addition of Formic Acid

Initial Concentration (µg/L)	Calculated	Observed	Agreement
0.8	1.6	1.8	1.12
1.0	2.0	2.1	1.05
1.1	2.2	2.3	1.04
1.1	2.2	2.2	1.00

Standard addition was also used to confirm the identification of the chromatographic peaks based on comparison of retention time. No interference was observed due to chloride, sulfate, or carbonate ion. Both formate and acetate were adequately resolved. A small unidentified peak did precede formic acid but did not significantly affect quantitation (Figure 20).

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Two ion chromatographic techniques were evaluated to quantify carboxylic acids. A commonly utilized anion separation system utilizing a carbonate eluent inadequately separated all acids of interest. It was also affected by the presence of strong acids (e.g., HNO_3) during subsequent consecutive analyses.

In order to preclude this problem, an ion chromatography exclusion scheme was evaluated. Samples collected in a mine environment were analyzed on an ICE system with dilute hydrochloric acid eluent. The precision of the ICE method was experimentally determined to be ± 2.5%. The accuracy was not indepently determined, but good precision and recovery yield confidence that measured values are within ±5% of the true value. No interferences were observed in the ICE system due to strong acids, carbonic acid or other water soluble species present in mine air subject to diesel emissions.

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TABLE 20

Analytical Data for Dicarboxylic Acids

(MEG Category 8B)

Compound	Composition	MW	pK_1	Retention Time (min)	Relative Sensitivity[a]	Lower Limits of Analysis (ppm)[b]
Oxalic	$(COOH)_2$	90	1.23	38.1±0.6	63	0.16
Malonic	$COOHCH_2COOH$	104	2.83	20.7±0.4	100	0.1
Maleic	Cis-COOHCHCHCOOH	116	1.83	23.9±0.3	78	0.13
Succinic	$COOH(CH_2)_2COOH$	118	4.16	16.2±0.4	44	0.23
Glutaric	$COOH(CH_2)_3COOH$	132	4.34	14.9±0.4	27	0.37
Adipic	$COOH(CH_2)_4COOH$	146	4.43	15.0±0.4	18	0.56
Pimelic	$COOH(CH_2)_5COOH$	160	4.71	15.5±0.2	~10	~1.0
Suberic	$COOH(CH_2)_6COOH$	174	4.52	19.3±0.2	~10	~1.0

(a) Using Malonic acid as 100% and peak height data

(b) Estimated using the requirement of 0.005 μMho response for detection

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Sample:		Peak No.
	1 ppm Glutaric	1
	1.4 ppm Succinic	2
	0.9 ppm Maleic	3
	1.3 ppm Oxalic	4

Column: Two 3 x 500mm Anion Separator

Eluent: 0.008 M Na_2CO_3 in 25% aqueous MeOH

Flow Rate: 1.45 mL/min. (19% flow)

Sensitivity: 1 μMho full scale

Chart Speed: 1.0 cm per 6 minutes

Sample Size: 100 μL

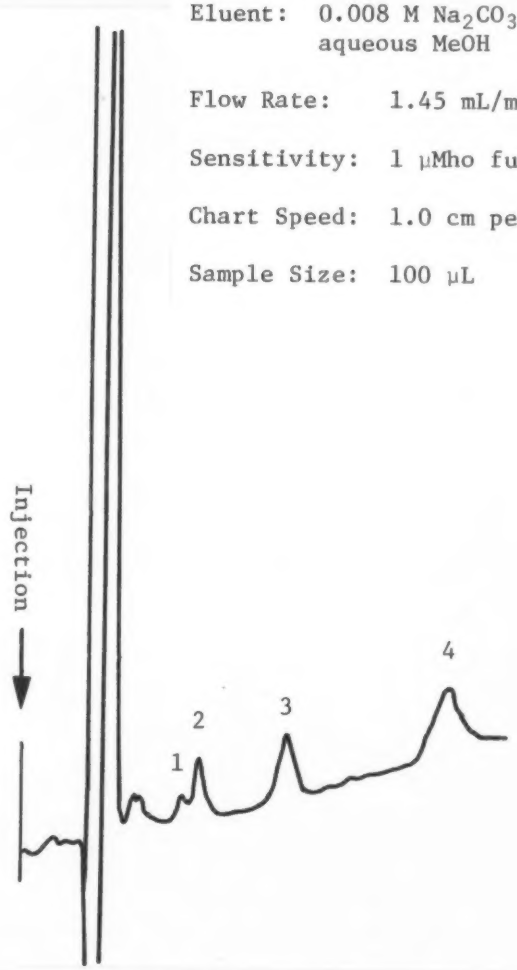

Figure 15. IC Chromatogram of Dicarboxylic Acids

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		Peak No.
Sample:	4 ppm Glutaric	1
	3 ppm Adipic	1
	2.8 ppm Succinic	2
	3.9 ppm Malonic	3
	3.3 ppm Fumaric	3
	3.4 ppm Maleic	4
	8.3 ppm Oxalic	5

Conditions: Same as Figure 15

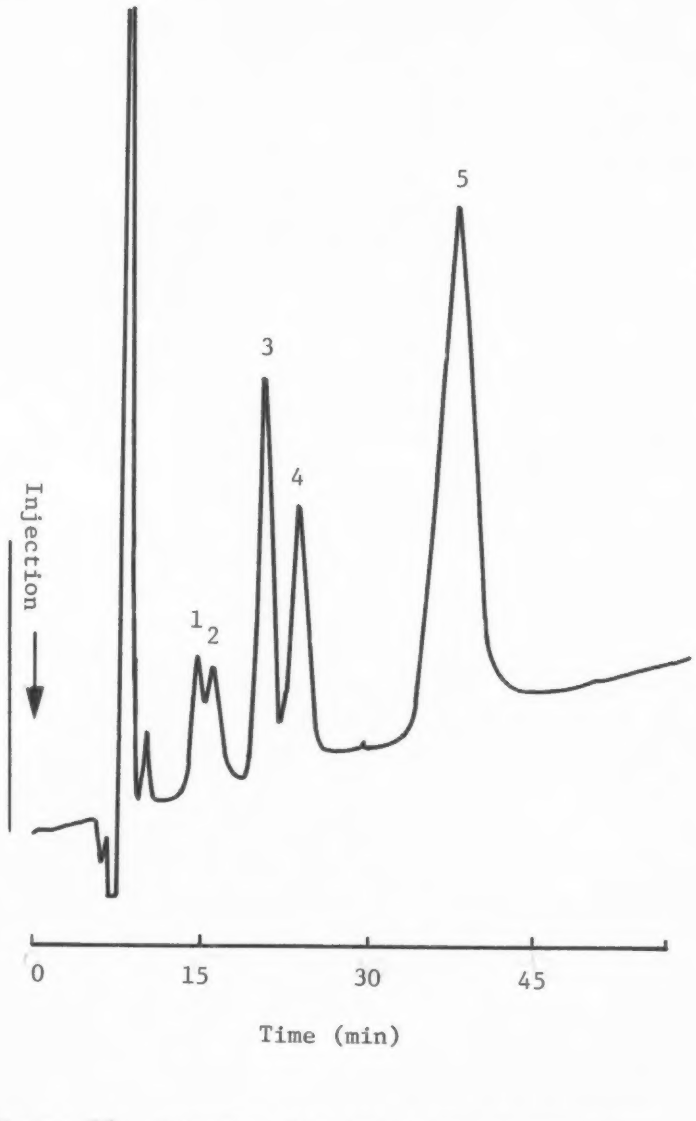

Figure 16. Dicarboxylic Acids Ion Chromatogram

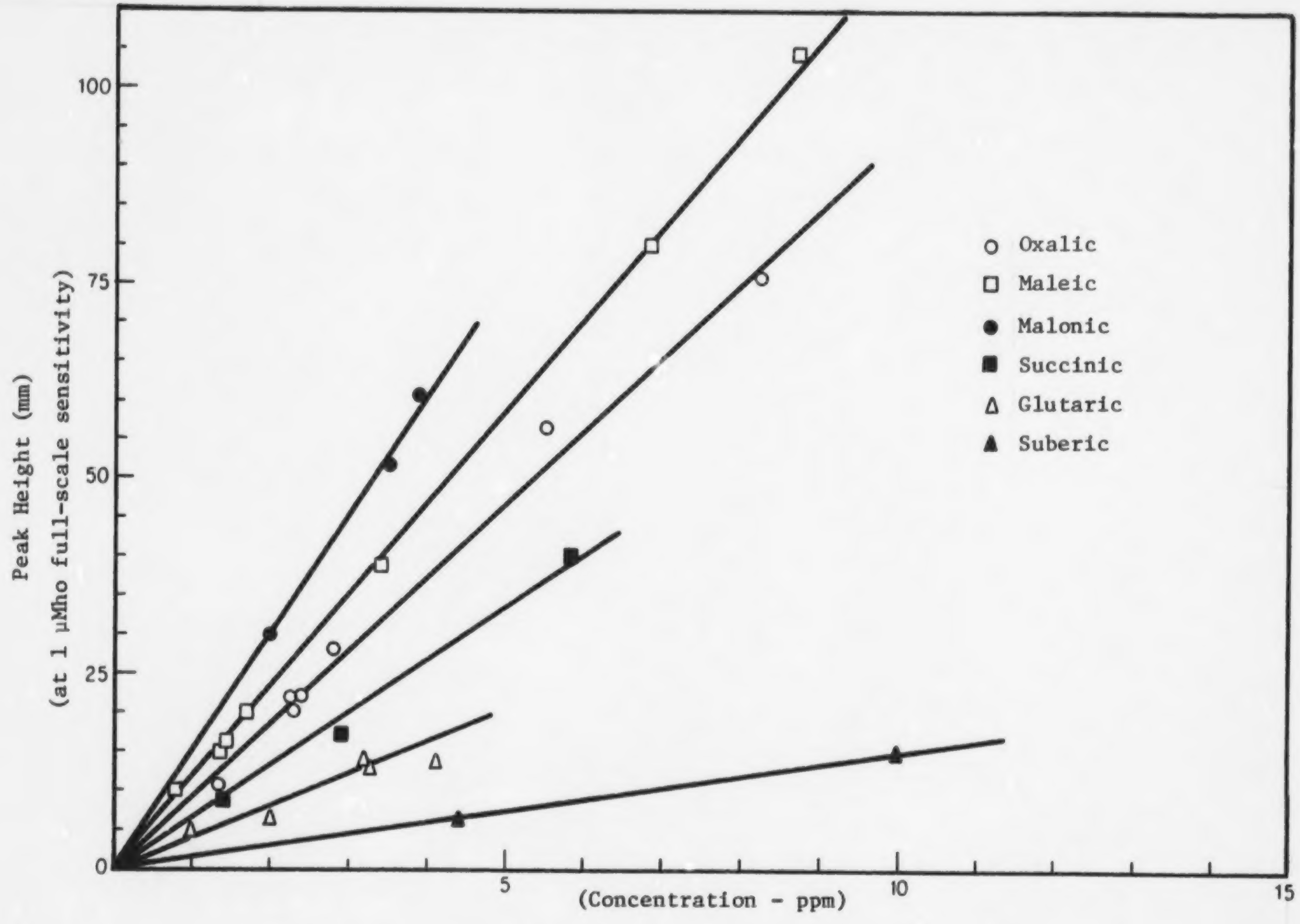

Figure 17. Calibration Curves for Various Dicarboxylic Acids

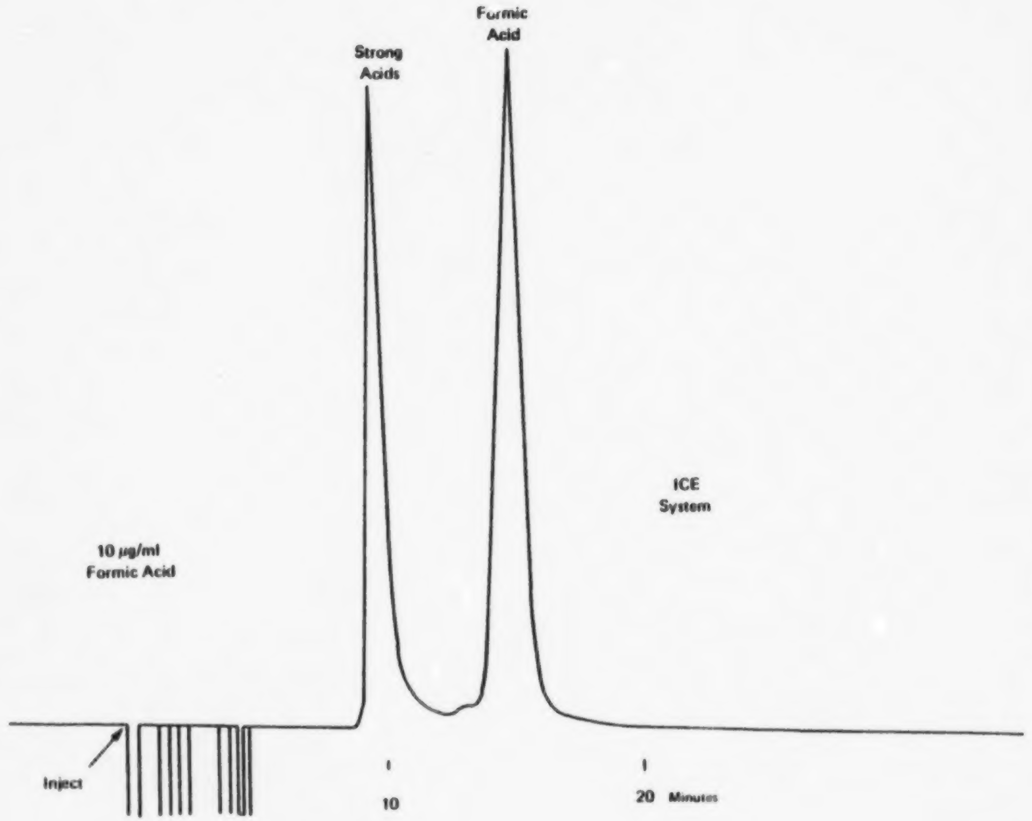

Figure 18. ICE Chromatogram of Formic Acid and Other Strong Acids

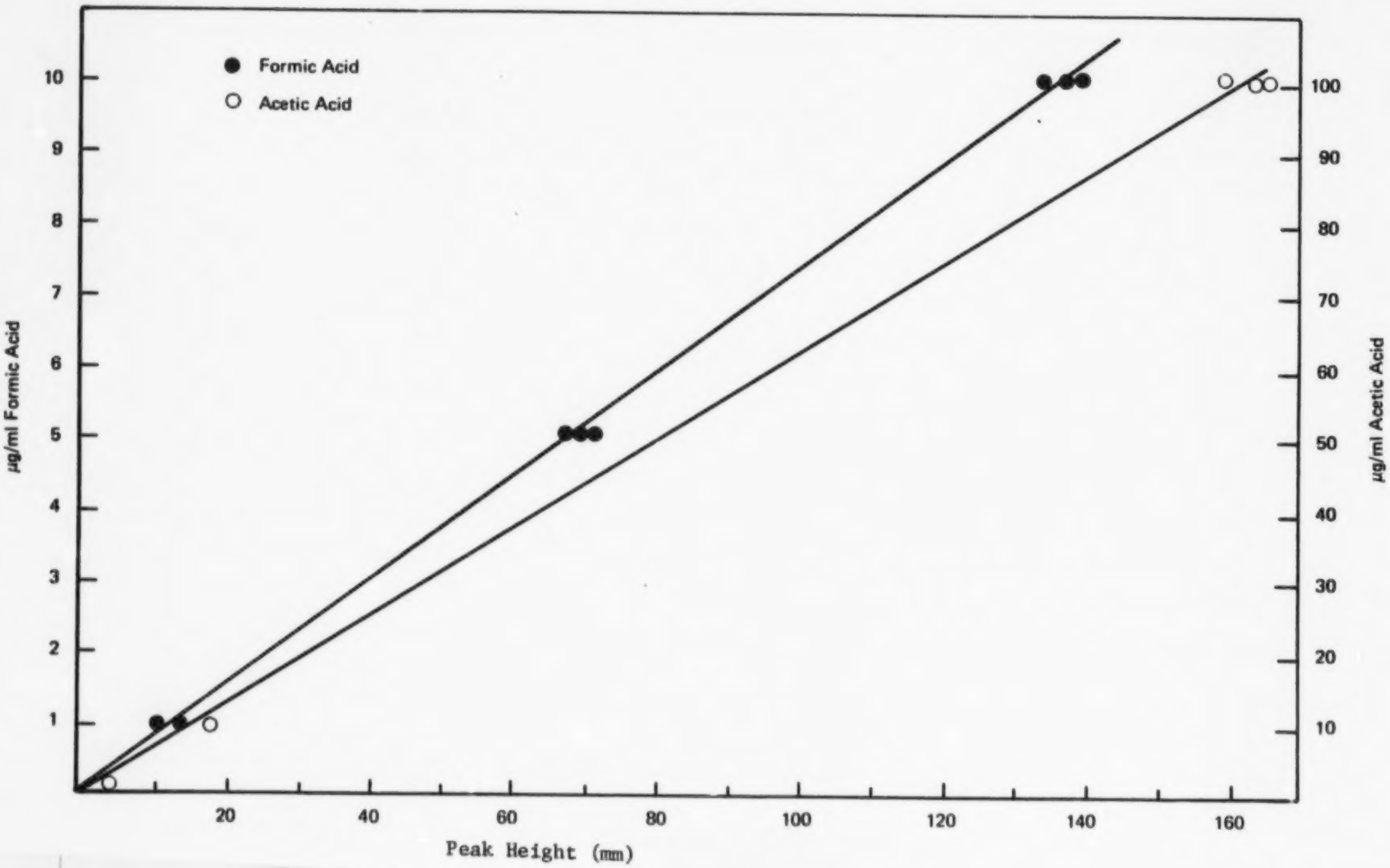

Figure 19. Standard Curve for ICE System

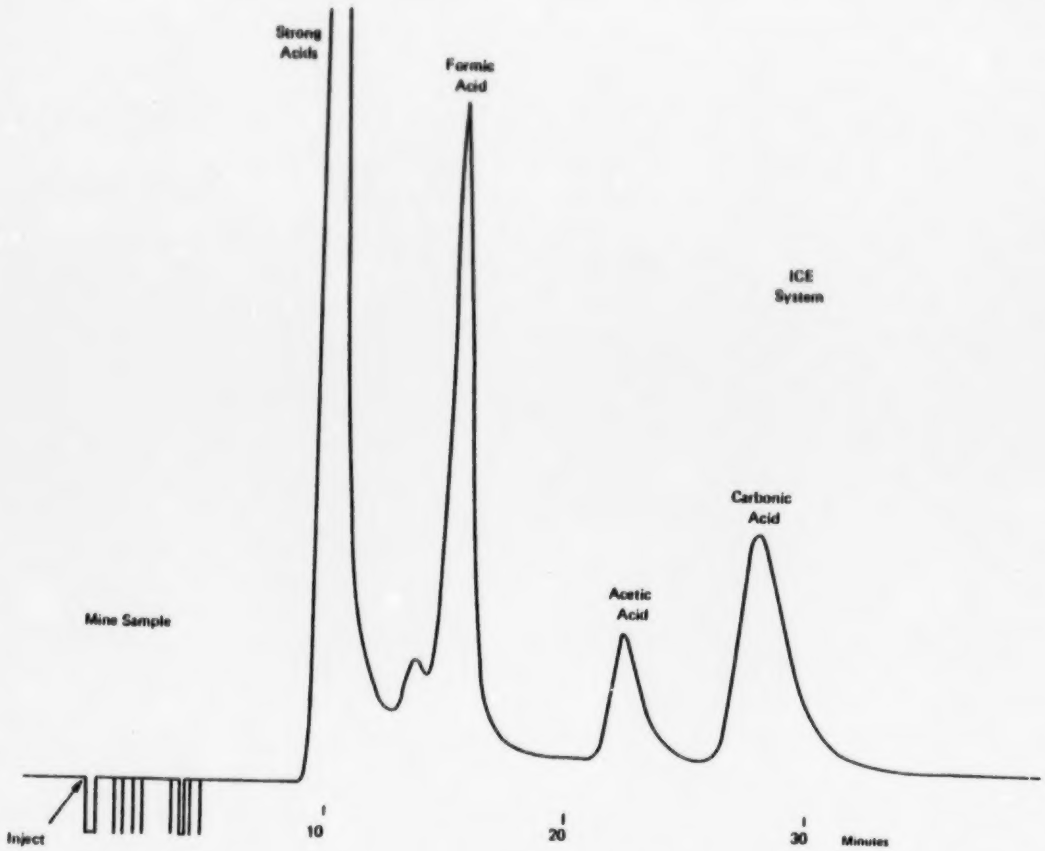

Figure 20. Chromatogram of Mine Sample

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Amides (MEG Category 8C)

The analytical method recommended for the amides category is gas chromatography/mass spectroscopy. This method has not been evaluated during this program.

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AMIDES - (MEG CATEGORY 8C)

Recommended Method

Recommended Method: GC/MS

Column: 3% Dexsil 400 on 100/120 mesh Supelcoport, 3m x 2mm glass column

Example Conditions: Flow Rate: 20 mL/min.

Column Temperature: 150°C
↓ 8°C/min.
300°C

Detection Limit: 50 ng injected

Suggested Alternative Method

1. GC/NPD (nitrogen-phosphorous detector) is an alternative detection system for amides. The following conditions are for the analysis of formamide:

    Column: Chromosorb 101, 1.8m x 2mm stainless steel

    Example Conditions: Carrier Gas: 45 mL/min., Helium

    Column Temperature: 190°C (isothermal)

    Injector: 225°C

    NPD Detector:
    Rh Bead Amplifier Setting: 450
    Air Flow: 26 psi
    Hydrogen Flow: 10 psi

    The retention time of formamide (composition - CH_3NO, MW = 45, b.p. 210°C), using the above conditions is approximately 3 minutes. The reported detection limit $\leq$ 10 mg/L in water, with 1 to 2 μL of aqueous sample injected. This procedure should also be applicable for the analysis of other amides such as acetamide (C_2H_5NO, MW = 59, b.p. 221°C). (Reference 28).

Reference

28. Millipore: "Test Method, Formamide in Water," 5/23/80.

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Esters (MEG Category 8D)

The analytical method recommended for the esters category (MEG Category 8D) is gas chromatography/mass spectroscopy.

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ESTERS - (MEG CATEGORY 8D)

Recommended Method

Recommended Method: GC/MS

Column: 3% SP 2250 on 100/120 mesh Supelcoport
2m x 2mm glass column

Example Conditions: Carrier Gas: 20 mL/min., Helium

Column
Temperature: 75°C
↓ 8°C/min.
325°C

Injector: 250°C

Lower Limit of Analysis: 50 ng injected

Suggested Alternative Methods

1. GC/FID (same chromatographic conditions as above), or GC/ECD are alternative detection systems for preliminary evaluation or for interference free samples.

   Flame Ionization Lower Limit of Analysis: 50 ng injected, except dioctyl phthalate - 10 ng injected

   Electron Capture Lower Limit of Analysis: <1 ng injected for phthalates

2. An alternative column is:

   Column: 1.5% SP 2250 + 1.95% SP 2401 on 100/120 Supelcoport, 1.8m x 4mm glass

   ECD Temperature: 300°C

   Carrier Gas: 60 mL/min., 5% Methane/95% Argon (Reference 29)

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Column Temperature	Compound	Detection Limit (ng injected)	RRT*
180°C	Dimethyl Phthalate	.05	.37
	Diethyl Phthalate	.06	.51
	Dibutyl Phthalate	.08	1.58
	Aldrin (IS)		1.00
220°C	Butylbenzyl Phthalate	.002	3.77
	bis(2-ethylhexyl)Phthalate	.04	4.85
	Dioctyl Phthalate	.13	8.80
	Aldrin (IS)		1.00

*Relative Retention Time - relative to aldrin, RT = 5.49 min. at 180°C, and RT = 1.84 min. at 220°C.

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Reference

29. Federal Register, Vol. 44, No. 233, Monday, December 3, 1979, pp. 69491-69494.

ESTER COMPOUNDS - (MEG Category 8D)

Method Evaluation

The analytical method originally recommended for Esters (MEG Category 8D) in the Level 2 Sampling and Analysis Manual was:

Column: 3% SP 2250 on 100/120 mesh Supelcoport
2m x 2mm glass column

Example Conditions: 20 mL/min.

Column
Temperature: 100°C
↓ 6°C/min.
280°C

The analytical finish for the ester compounds was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph. The recommended GC column, 3% SP 2250 on 100/120 mesh Supelcoport, was conditioned overnight at 350°C.

A test mixture was prepared consisting of the compounds listed in Table 21 in methylene chloride. This mixture was chromatographed on the 3% SP 2250 GC column, using the recommended conditions, to determine whether the individual compounds were adequately resolved.

The original method recommended that the column be temperature programmed from 100°C to 280°C at 6°C per minute. This was changed to temperature programming from 75°C to 325°C at 8°C per minute. The change to a lower initial temperature was made to resolve the GC peaks of the low boiling esters, i.e., isobutyl acetate, b.p. 118°C and diethyloxalate, b.p. 186°C, from the GC peak of the solvent, methylene chloride. The GC peak of isobutyl acetate still was not completely resolved from the solvent GC peak. Diethyloxalate and methyl benzoate GC peaks were also not adequately resolved. Lowering the initial column temperature below 75°C caused considerable peak broadening, and was therefore not considered useful. The change in the programming rate to 8°C per minute was made in order to compensate for the GC peak broadening caused by the lowering of the intial column temperature from 100°C to 75°C. The upper temperature limit was increased from 280°C to 325°C to elute dioctyl phthalate. A representative gas chromatogram is presented in Figure 21.

It was necessary to determine the GC peak retention times of each ester in the test mixture. The retention times were determined by sequentially adding each of the esters to methylene chloride and chromatographing the solution after each addition. The retention times for each ester compound in the test mixture are listed in Table 21.

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The detection limit for each ester compound was determined. Four test mixtures in methylene chloride, corresponding to concentrations of 300 ng/μL, 150 ng/μL, and 10 ng/μL were prepared and chromatographed using the revised recommended conditions.

Dioctyl phthalate was the only ester easily detected at 10 ng injected on the column. The other six ester compounds were detected with some difficulty at 50 ng injected on the column. The higher detection limit for the six ester compounds with boiling points less than 200°C were partially caused by interferences due to the methylene chloride GC peak tailing and extraneous GC peaks attributable to the 3% SP 2250 GC column. This difficulty might be overcome by using GC/MS techniques, in which specific ions can be monitored.

Evidence concerning the precision and accuracy of this method of analyzing ester compounds is available from other programs. In one study[10], a mixture of compounds, including five ester compounds, was added into clean water and to raw municipal wastewater to give a concentration level of 50 μg/L. One liter aliquots of the water samples, adjusted to a pH greater than 11, were extracted three times with methylene chloride (250 mL, 100 mL, 100 mL). These extracts were then analyzed by GC/MS, using a 3% SP 2250 DB GC column. The observed detection limit for each ester compound using GC/MS was 10 ng injected. Concentration values were calculated relative to an internal standard. The average recoveries ($\bar{P}$) and standard deviations (Sp) of replicate analyses for the six compounds follow:

	Clean Water[(a)]		Raw Municipal Wastewater[(b)]	
	$\bar{P}$	Sp	$\bar{P}$	Sp
Dimethyl Phthalate	62	18	70	27
Diethyl Phthalate	77	18	94	27
Di-n-butyl Phthalate	96	15	69	56
Butylbenzyl Phthalate	75	9	47	15
Bis(ethyl-hexyl)Phthalate	52	12	50	14
Di-n-octyl Phthalate	52	12	50	14

(a) Based on 7 Data Points.

(b) Based on 14 Data Points.

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TABLE 21

Analytical Data for Esters

(MEG Category 8D)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC Peak No.[a]	RRT[b]
8D	Isobutyl Acetate	$C_6H_{12}O_2$	116	118	1	.28
8D	Diethyl Oxalate	$C_6H_{10}O_4$	146	186	2	.78
8D	Methyl Benzoate	$C_8H_8O_2$	136	200	3	.83
8D	Methyl Salicylate	$C_8H_8O_3$	152	220-4	4	1.00
8D	Ethyl Adipate	$C_{10}H_{18}O_4$	202	240-5	5	1.5
8D	Dimethyl Phthalate	$C_{10}H_{10}O_4$	194	284	6	1.69
8D	Dioctyl Phthalate	$C_{24}H_{38}O_4$	390	384	7	3.17

(a) Numbers refer to Figure 21.

(b) Relative Retention Times (relative to methyl salicylate, RT = 10 min.).

ering

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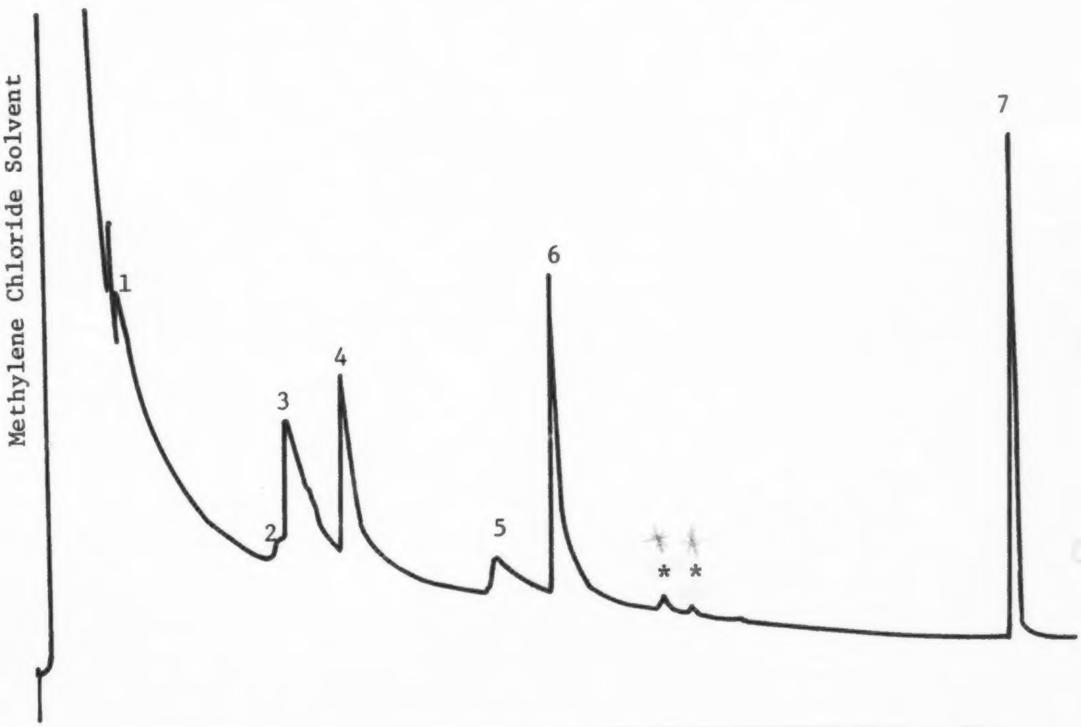
Sample:	∿300 nanograms each ester compound in 1.0 μL methylene chloride
Column:	3% SP 2250, 100/120 Supelcoport, 2m x 2mm glass
Column Temperature:	$75^\circ\text{C} \xrightarrow{8^\circ\text{C/min.}} 325^\circ\text{C}$
FI Detector Temperature:	300°C
Injector Temperature:	250°C
Flow Rate:	20 mL/min., Helium
Attenuation x Range:	2×10^{-11} amp/mV
Chart Speed:	0.5 cm/min.



* GC peaks due to interference from GC column.

(GC peaks numbers refer to Table 21)

Figure 21. Gas Chromatogram of Esters

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Nitriles (MEG Category 9)

The compounds in the nitrile category (MEG Category 9) include both aliphatic and aromatic nitriles. The analytical method recommended for this category is gas chromatography/mass spectroscopy.

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NITRILES - (MEG CATEGORY 9)

Recommended Method

Recommended Method: GC/MS

Column: 3% SP 1000 on 100/120 mesh Supelcoport, 2m x 2mm glass

Example Conditions: Carrier Gas: 20 mL/min., Helium

Column Temperature: 35°C (6 min.)
$\downarrow$ 10°C/min.
250°C

Injector Temparature 275°C

Lower Limit of Analysis: 50 ng injected, except malononitrile - 150 ng injected

Suggested Alternative Methods

1. Flame Ionization Detection can be used for interference-free samples.

   FID Temperature: 300°C

   GC/FID Lower Limit of Analysis: 10 ng injected, except malononitrile - 150 ng injected. Acrylonitrile, and allyl cyanide can be detected at 50 ng injected if there is no diluting solvent, i.e., gas samples or purge and trap techniques. If a diluting solvent is presented (e.g., CH_2Cl_2), limits are 250 ng, 1 µg, and 75 ng, respectively.

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NITRILES - (MEG CATEGORY 9)

Method Evaluation

The analytical method originally recommended for nitriles in the Level 2 Sampling and Analysis Manual was:

Column: 3% SP 1000 on 100/120 Supelcoport
2m x 2mm glass

Example Conditions: Flow Rate: 30 mL/min.

Column Temperature: 100°C

$$\downarrow 8^\circ\text{C/min.}$$

250°C

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph. The recommended GC columm, 3% SP 1000 on 100/120 mesh Supelcoport, was conditioned overnight at 300°C.

A test mixture was prepared consisting of the compounds listed in Table 22 in methylene chloride. The test mixture was chromatographed on the 3% SP 1000 GC column, using the recommended conditions, to determine whether the individual compounds were adequately resolved. The original method recommended a temperature program of 100°C $\xrightarrow{8^\circ\text{C/min.}}$ 250°C. This was changed to a temperature program of 35°C (isothermal, 6 minutes) $\xrightarrow{10^\circ\text{C/min.}}$ 250°C. The initial temperature was lowered and the six-minute isothermal hold was introduced to resolve acrylonitrile (b.p. 77°C) and acetonitrile (b.p. 81°C) from the methylene chloride solvent peak. Resolving the low boiling nitrile compound GC peaks from the methylene chloride GC peak will not typically be necessary since these compounds will either be collected as a gas sample or analyzed using purge and trap techniques. The temperature rate was increased to 10°C/min. to reduce the GC peak broadening and tailing observed at 8°C/min.

It was necessary to determine the GC peak retention time of each nitrile compound in the test mixture. The retention times were determined by sequentially adding each of the compounds to methylene chloride and chromatographing the solution after each addition. Retention times for each of the compounds in the test mixture are presented in Table 22; a representative gas chromatogram is presented in Figure 22.

A lower limit of analysis for reliable quantification of each nitrile was determined. Test mixtures were prepared in methylene chloride corresponding to various concentration levels of each compound. These test mixtures were chromatographed using the revised recommend conditions.

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The lower limits of analysis, reported in ng injected on column, for each nitrile compound in the test mixture were found to vary, as shown:

Acrylonitrile	250 ng injected
Acetonitrile	1,000 ng
Allyl Cyanide	75 ng
Hexanonitrile	10 ng
n-Heptyl Cyanide	5 ng
Cycloheptyl Cyanide	5 ng
Benzyl Cyanide	5 ng
Malononitrile	150 ng

The lower limits for acrylonitrile (b.p. 77), acetonitrile (b.p. 81), and allyl cyanide (b.p. 119) would be somewhat improved if these compounds were analyzed in a gas sample or in a water sample using purge-and-trap techniques.

Acrylonitrile is routinely analyzed in other programs[10] using purge-and-trap/gas chromatography/mass spectroscopy. In these programs, a routine quality control program is maintained in which a mixture of compounds, including acrylonitrile, is added to wastewater to give a concentration level of 100 μg/L. Five milliliter aliquots of the aqueous sample at 50°C are purged with helium for four minutes onto a Tenax/charcoal trap. The trap is subsequently purged for four minutes at 180°C onto a 6 ft. x 1/8 inch I.D. glass GC column packed with 80/100 Carbopack C, 0.2% Carbowax 1500. The GC column is interfaced with a Finnegan 4000 Mass Spectrometer.

The observed lower limit of analysis using this PAT/GC/MS technique is 1 μg/L. Analytes are quantified using calibration curves constructed from the results of analyzing purged aqueous calibration solutions. The average recovery of acrylonitrile from raw municpal wastewater was 94% with a range of relative standard deviations from 8% to 24%. These data were collected over a period of two years.

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TABLE 22

Analytical Data for Nitriles

(MEG Category 9)

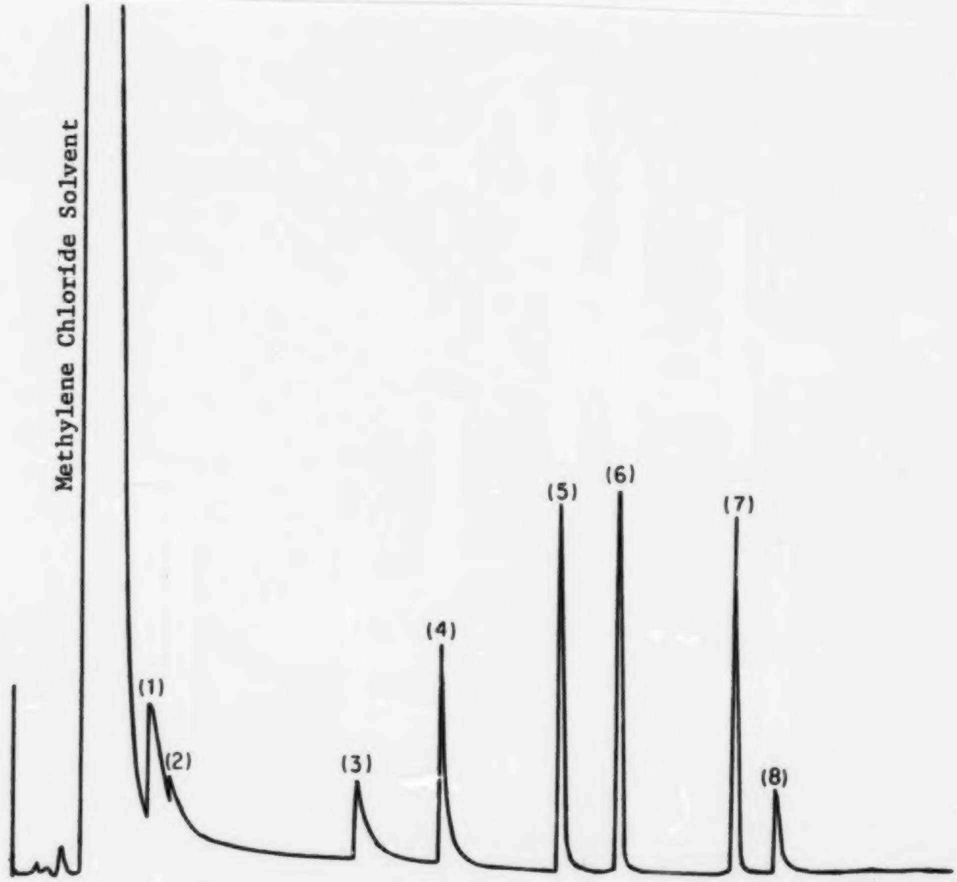
MEG Category No.	Compound	Composition	MW	BP(°C)	GC[a] Peak No.	RRT[b]
9	Acrylonitrile	CH_2:CHCN	53	77	1	0.26
9	Acetonitrile	CH_3CN	41	81	2	0.29
9	Allyl Cyanide	CH_2:$CHCH_2CN$	67	119	3	0.63
9	Hexanonitrile	$CH_3(CH_2)_4CN$	97	164	4	0.78
9	n-Heptylcyanide	$CH_3(CH_2)_6CN$	125	198-200	5	1.00
9	Cycloheptylcyanide	$C_7H_{13}CN$	123	85-86/10mm	6	1.11
9	Benzylcyanide	$C_6H_5CH_2CN$	117	234	7	1.32
9	Malononitrile	$CH_2(CN)_2$	66	220	8	1.39

(a) Numbers refer to gas chromatogram, Figure 22.

(b) Relative Retention Times (relative to n-heptylcyanide, RT = 16.2 minutes).

x 11

Sample:	500 nanograms of each compound, except 1 μg acrylonitrile, 2 μg acetonitrile, 1.6 μg malononitrile, in 1 μL methylene chloride
Column:	1% SP 1000 on 100/120 mesh Supelcoport, 2m x 2mm glass
Flow Rate:	20 mL/min., Helium
Column Temperature:	35°C (6 min.) $\xrightarrow{10^\circ\text{C/min.}}$ 250°C
Injector Temperature:	275°C
FID Temperature:	300°C
Attenuation x Range:	8 x 10^{-11} amp/mV
Chart Speed:	0.5 cm/min.



(GC peak numbers refer to Table 22)

Figure 22. Gas Chromatogram of Nitriles

The precision and accuracy of the overall nitrile analysis method were investigated. A mixture of nitriles, 6 mg each in 50 µL methylene chloride, listed in Table 23, were added to 20 grams of XAD-2. This concentration level was chosen as an appropriate level of interest when using XAD-2 to sample nitriles as vapors. Four replicate XAD-2 samples were Soxhlet extracted with 200 mL of methylene chloride for 24 hours. These extracts were concentrated using a Kuderna Danish evaporator. The concentrated extracts were analyzed by GC/FID on 3% SP 1000, 100/120 Supelcoport, using the recommended conditions described previously. The recoveries $(\bar{P})$ and standard deviation (Sp) of replicate analyses after the extraction and concentration are listed in Table 23. The recoveries and precision are good. The recovery losses are probably associated with the concentration step.

The extracts were then chromatographed on silica gel using the procedure described in the IERL:RTP Procedures Manual; Level 1 Environmental Assessment (Second Edition), October 1978. Pentadecane and naphthalene were also added to these extracted samples to verify the silica gel elution pattern. The seven silica gel fractions were analyzed using GC/FID, as previously described. Fractions 4 and 5 were found to contain the nitriles, with more eluting in Fraction 4. Pentadecane eluted in Fraction 1 and naphthalene eluted in Fraction 2, confirming that the silica gel column was giving an appropriate elution pattern.

The overall recovery data for the extraction/concentration/silica gel procedure are presented in Table 23. It was not possible to detect malononitrile after silica gel chromatography. This compound is unstable and probably degraded during silica gel chromatography.

The recoveries from silica gel are low, but reproducible. A correction factor could probably be used when calculating sample concentration levels of hexanonitrile, n-heptylcyanide, cycloheptylcyanide, and benzyl cyanide. However, the recovery is so poor for allyl cyanide that silica gel clean-up probably should be avoided when possible. The poor recovery is probably due to allyl cyanide being volatile. Silica gel clean up must also be avoided when analyzing for malononitrile.

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TABLE 23

Recovery Data for Nitriles Using XAD-2 and Silica Gel

(MEG Category 9)

Compound	BP°C	XAD-2 Extraction Concentration			XAD-2 Extraction Concentration, Silica Gel		
		P^1	$\overline{P}^2$	Sp^3	P^1	$\overline{P}^2$	Sp^3
Allyl Cyanide	119	80 75 85 85	81	4.8	6 24 16 26	18	9.2
Hexanonitrile	164	82 75 84 85	82	4.5	21 41 32 46	35	11
n-Heptyl Cyanide	198-200	84 77 84 86	83	3.9	36 53 44 45	44	7
Cycloheptylcyanide	85-86(10 mm)	85 78 86 87	84	4.1	47 57 50 64	54	8
Benzyl Cyanide	234	86 81 89 91	87	4.4	55 63 75 75	62	10
Malononitrile	220	80 80 88 91	85	5.6	Could not be detected		

[1] P - Recovery
[2] $\overline{P}$ - Average recovery based on 4 data points
[3] Sp - Standard deviation for the average recovery

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Amines (MEG Category 10)

The compounds included in the amine category (MEG Category 10) are primary, secondary, and tertiary amines. The analytical method for this category is gas chromatography/mass spectroscopy.

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AMINES - (MEG CATEGORY 10)

Recommended Method

Recommended Method: GC/MS

For Species with Boiling Point Ranges from 100°C to 210°C

Column: 4% Carbowax 20M on Carbopack B + .8% KOH
2m x 2mm glass column

Note: GC column must be conditioned with 10 µL injections of water over a half-hour before using the column

Example Conditions: Carrier Gas: 20 mL/min., N_2

Column Temperature: 180°C

↓ 5°C/min.

200°C (10 min.)

Note: Do not substitute helium as the carrier gas.

Injector: 220°C

Suggested Alternative Methods

1. GC/FID for samples free of interferences or preliminary evaluation.

   Flame Ionization Detector Temperature: 220°C

   GC/FID Detection Limit: 20 ng injected, except m-toluidine - 35 ng injected

2. For high boiling amines:

   Column: 10% Carbowax 20M + 2% KOH on 80/100 Chromosorb WAW, 2m x 2mm glass column

   Column Temperature: 200°C

   Flow Rate: 20 mL/min.

   Retention Time for nicotine is approximately 3.2 min. (Reference 30)

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3. For non-volatile amines:

HPLC can be used. Young and McNair[31] have separated a wide variety of high-MW amines using several different silica gel columns.

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References

30. "Amine Analysis," Supelco Bulletin 737B, Supelco, Inc., Bellefonte, PA.

31. Young, P.R., and H.M. McNair, "High Pressure Liquid Chromatography of Aromatic Amines," Journal of Chromatography, 119 (1978) 569-579.

AMINES - (MEG CATEGORY 10)

Method Evaluation

The analytical method originally recommended for amines (MEG Category 10) with boiling points from 100°C to 210°C in the Level 2 sampling and Analysis Manual was:

Column:	4% Carbowax 20M on Carbopack B + .8% KOH 2m x 2mm glass column
Example Conditions:	Carrier Gas: 20 mL/min. N_2
	Column Temperature: 100°C $\xrightarrow{8^\circ C/\text{min.}}$ 200°C

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Hewlett Packard 5840A Gas Chromatograph.

The recommended GC column was conditioned by heating at 220°C overnight and subsequently injecting 10 µL aliquots of water over a one-half hour period. (This is intended to convert any potassium carbonate in the stationary phase back to potassium hydroxide).

A test mixture was prepared consisting of the amine compounds listed in Table 24, in methylene chloride. This test mixture was chromatographed at the recommended conditions on the 4% Carbowax 20 M/Carbopack B + .8% KOH GC column, to determine whether the individual amine compounds were adequately resolved. The original method recommended a column temperature program from 100°C to 200°C at 8°C per minute. This was changed to a GC column temperature program from 180°C to 200°C (isothermal 10 min.) at 5°C per minute, because the lowest boiling amine compound, dipropylamine (109°C), eluted in 12 minutes using the original conditions. The analysis time was shortened by approximately 5 minutes using the revised GC column temperature program. It might be possible to find an isothermal GC condition that would suffice to resolve any particular mix of compounds tested. However, for general Level 2 purposes, it seems worthwhile to maintain the flexibility of the temperature programmed mode.

It was necessary to determine the GC peak retention times of each amine compound in the test mixture. The retention times were determined by sequentially adding each of the amine compounds to methylene chloride and chromatographing the solution after each addition. Retention times for each of the amine compounds in the test mixture are presented in

Table 24. A representative gas chromatogram is presented in Figure 23. Dibutylamine and o-toluidine were not resolved. However, in GC/MS analysis, appropriate ions could be monitored by mass spectroscopy to distinguish the two compounds, or the GC conditions could be modified to effect separation.

The lower limit of analysis for each amine compound was determined. Three test mixtures were prepared at concentrations corresponding to 70 ng/μL, 35 ng/μL, and 21 ng/μL for each amine compound.

The individual amine compounds were easily detected at approximately 20 nanograms injected on the column, except m-toluidine which was detected at 35 nanograms.

In some preliminary work with the 4% Carbowax 20M/Carbopack B + .8% KOH GC column, helium was used as the carrier gas rather than nitrogen. The use of helium as the carrier gas resulted in extraneous GC peaks; therefore helium should not be substituted as the carrier gas.

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TABLE 24

Analytical Data for Amines

(MEG Category 10)

MEG Category No.	Compound	Composition	MW	BP (°C)	GC Peak No.(a)	RRT(b)
10B	Dipropyl Amine	$(C_3H_7)_2$ NH	101	109	1	.32
10A	Aniline	C_6H_5 NH_2	93	184	2	.62
10B	Disecbutyl Amine	$(C_4H_9)_2$ NH	129	135	3	.76
10C	Tripropyl Amine	$(C_3H_7)_3$ N	143	156	4	1.00
10B	Dibutyl Amine	$(C_4H_9)_2$ NH	129	159	5	1.14
10A	O-Toluidine	C_7H_7 NH_2	107	200	6	1.14
10A	M-Toluidine	C_7H_7 NH_2	107	203	7	1.28

(a) Numbers refer to gas chromatogram, Figure 23.

(b) Relative Retention Times (relative to tripropyl amine, RT = 10.25 min.)

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Sample: 50 nanograms each amine compound in 1.0 µL methylene chloride

Column: 4% Carbowax 20 M on Carbopack B + 0.8 KOH, 2m x 2mm glass column

Column Temperature: $180^\circ\mathrm{C} \xrightarrow{5^\circ\mathrm{C/min.}} 200^\circ\mathrm{C}$ (10 min. isothermal)

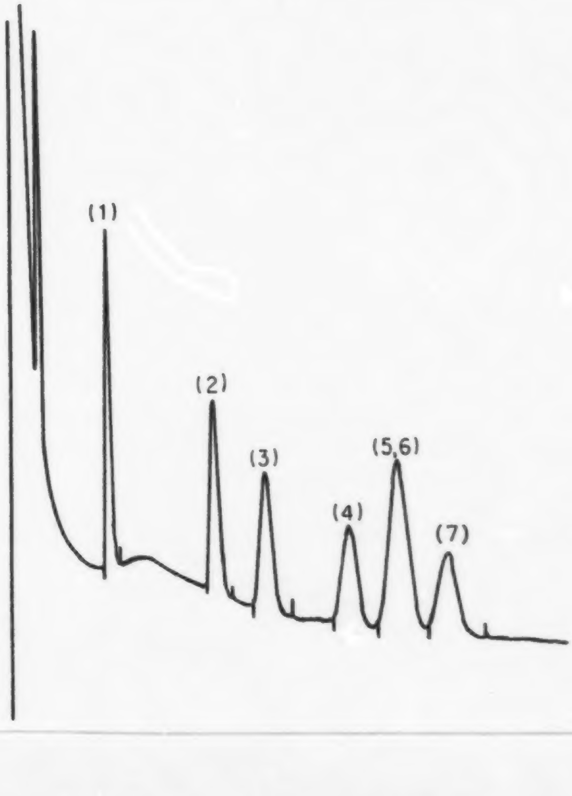
Carrier Gas: 20 mL/min, N_2

Injector Temperature: 220°C

FI Detector Temperature: 280°C

Attenuation Range: 2^6

Chart Speed: 0.50 cm/min.



(GC peak numbers refer to Table 24)

Figure 23. Gas Chromatogram of Amines

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Azo Compounds, Hydrazines, and Derivatives (MEG Category 11)

The analytical method recommended for the azo compounds, hydrazine, and derivatives (MEG Category 11) is a colorimetric technique. A derivatization-GC procedure for hydrazines looks promising and is suggested as an alternative method.

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AZO COMPOUNDS, HYDRAZINE, AND DERIVATIVES (MEG CATEGORY 11)

Recommended Method

The recommended method for this category is an approved NIOSH method for phenylhydrazine and 1,1-dimethylhydrazine and is expected to be general for all hydrazines. (Reference 32)

The collected sample is reacted with phosphomolybdic acid to form a complex with a strong adsorption maximum at 750 nm. The detection limit is approximately 5 mg/m^3 in air.

Suggested Alternative Method

A derivatization technique for hydrazines has been reported[33,34]. Hydrazines are derivatized using either acetone[33] or furfuraldehyde[34]. Gas chromarography with NPD[33], MS[33] or FID[34] detection is used as the analytical finish.

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References

32. NIOSH Manual of Analytical Methods, Second Edition, Method No. S160.

33. Selim, S., and C.R. Wanner, "Residue Determinations of Hydrazine in Water by Derivatization and Gas Chromatography", J. of Chrom., 166 (1978) 507-511).

34. Cook, L.R., R.E. Glenn and G.E. Podolak, "Monitoring and Analysis of Personnel Exposure to Hydrazines at a Rocket Propellant Plant", Am, Ind. Hygiene Assoc. Journal (40), 1/79, 69-77.

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AZO COMPOUNDS, HYDRAZONE, AND DERIVATIVES - (MEG CATEGORY 11)

Method Evaluation

The analytical method recommended for azo compounds, hydrazines and derivatives (MEG Category 11) in the Level 2 Sampling and Analysis manual is the approved NIOSH method for phenylhydrazine and 1,1-dimethylhydrazine[32]. This colorimetric technique, rather than a gas chromatographic technique, was recommended because the azo compounds and hydrazines may oxidize in air. It is anticipated that these reactive compounds would best be sampled by collection in an aqueous medium and, therefore, that an analysis method directly applicable to aqueous samples would be preferable.

In the NIOSH method, phenylhydrazine and 1,1-dimethylhydrazine in air samples are collected in hydrochloric acid and then reacted with phosphomolybdic acid (PMA) to form a bluish-green molybdenum-containing colored complex. This NIOSH method was evaluated by determining whether or not there were any deviations from Beer's Law, when analyzing phenylhydrazine and hydrazine. It was also determined if the absorbances for hydrazine and phenylhydrazine were additive. The instrument used for all quantitative colorimetric determinations was a Perkin Elmer Coleman 55 Spectrophotometer with a 1 cm cell path length.

It had previously been noted that, for some hydrazine compounds, the PMA reaction was slow at room temperature, i.e. there was an increase in the absorbance, at a given hydrazine concentration, with time. Feinsilver[35], determined that maximum color development for dimethylhydrazine reacting with PMA occurred when the reaction solution was heated. The effect of heating upon color formation was checked, using standard solutions of hydrazine and penylhydrazine. It was found experimentally that after heating the reaction solutions containing the PMA and hydrazine or phenylhydrazine for 1 hour at 75°C, the absorbances remained stable for up to 3 hours.

The reproducibility and linearity of calibration curves and any apparent deviations from Beer's Law were evaluated for both phenylhydrazine and hydrazine. Five test solutions of hydrazine and a reagent blank were prepared in 0.1N HCl, to which 15% w:v PMA solution was added. After these solutions had reacted for 1 hour at 75°C and cooled for 15 minutes at room temperature, the absorbance was read at 730 nm. The hydrazine concentrations in the PMA solution and absorbances are presented in Table 25. The corresponding calibration curve is presented in Figure 24. The slope of the hydrazine curve is .0084, therefore the molar absorptivity ($e = A/bc$, where e = absorptivity, A = absorbance, b = path length = 1 cm, c = concentration) is 8,400. The curve appears to be non-linear at concentration levels above 110 μM and at concentration levels below 30 μM. The y-intercept is non-zero, -0.083.

Five test solutions of phenylhydrazine and a reagent blank were prepared in 0.1N HCl and reacted with PMA. The μM concentration values for phenylhydrazine in the PMA solution are presented in Table 25. The absorbances were read at 730 nm, after allowing the solutions to react for 1 hour at 75°C. The absorbance values are presented in Table 25 and the corresponding calibration curve is presented in Figure 24. The slope of the phenylhydrazine curve is .0119, therefore the molar absorptivity at 730 nm is 11,900. The curve is linear from 15 μM to 50 μM. The y-intercept is non-zero, -.054 and the curve appears to be non-linear at levels less than 15 μM.

Hydrazine and phenylhydrazine were analyzed together to determine if the absorbances measured for the two compounds were additive. The calculated absorbances were determined by adding together the absorbance values measured for each hydrazine compound. The calculated and measured absorbance values are presented below:

Hydrazine Concentration μM	Phenylhydrazine Concentration μM	Calculated Absorbance	Measured Absorbance
61.4	20.80	.629	.660
71.6	24.3	.756	.766

The agreement between the calculated and measured results are good, i.e. within 5% (the estimated precision for the instrument used is 5%).

The detection limit for hydrazine and phenylhydrazine is approximated from the calibration curves (Figure 24) at 30 μM for hydrazine and 15 μM for phenylhydrazine in the PMA solution, which are equivalent to 96 μg of hydrazine/100 mL PMA solution and 162 μg of phenylhydrazine/ 100 mL of PMA solution. The aqueous sample aliquot was 85 mL, therefore, the detection limit for the original sample corresponds to 85 mLs or 1.13 mg/L of hydrazine or 1.90 mg/L of phenylhydrazine.

The negative y-intercepts for hydrazine and phenylhydrazine may indicate non-linearity at low concentrations. This may be interpreted as decreasing sensitivity at low concentrations. Additional work may lead to improvements in the detection limits and sensitivity of the procedure.

Interferences[32]

Any hydrazine derivative will potentially interfere with this method. Other reducing agents such as ferrous salts may also interfere. Further, aldehydes and ketones may interfere, because of the potential formation of phenylhydrazones in the acid medium in the bubbler. Other reported[33] interferences include hydroxylamine, urea, amino acids and amines.

TABLE 25

Analytical Data for Hydrazines

(MEG Category 11)

MEG Category No.	Compound	Composition	MW	BP, °C	Concentration μM	Absorbance,* 730 nm
11	Hydrazine	N_2H_4	32	113	20.4	.103
					40.8	.243
					61.3	.414
					123	1.014
					152	1.160
11	Phenylhydrazine	$C_6H_8N_2$	108	244 (decomposes)	6.94	.047
					13.87	.108
					20.80	.187
					41.61	.447
					48.55	.528

* Estimated precision of absorbance determinations with the instrumental system is on the order of 5%. Additional uncertainty may be associated with the variability in the color forming reaction process.

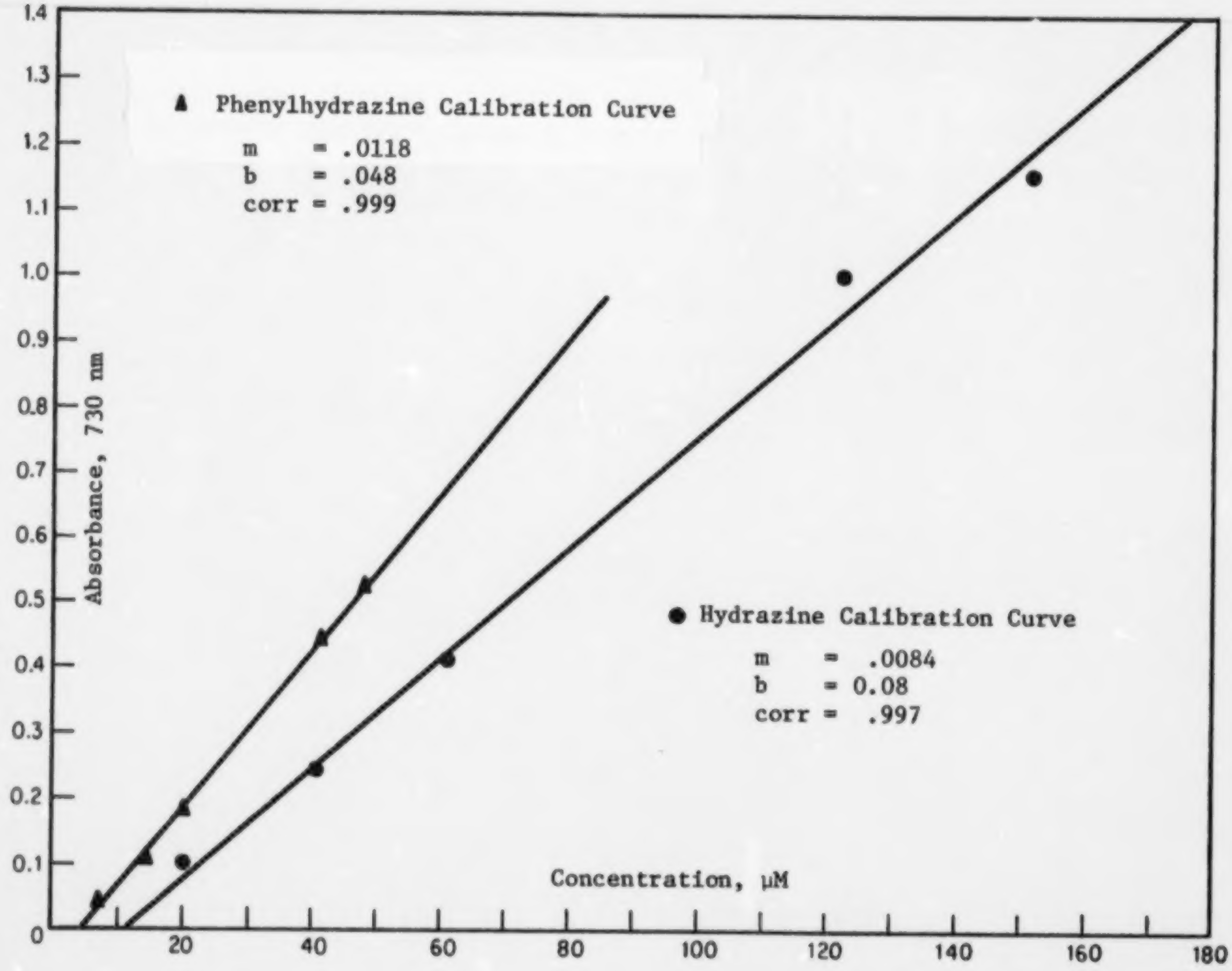

Figure 24. Calibration Curves for Hydrazines

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Nitrosamines (MEG Category 12)

The recommended analytical method for the nitrosamines (MEG Category 12) is gas chromatography/mass spectroscopy.

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NITROSAMINES - (MEG CATEGORY 12)

Recommended Method

Recommended Method: GC/MS

Column: 3% SP 2100 on 100/120 mesh Supelcoport
2m x 2mm glass column

Example Conditions: Carrier Gas: 20 mL/min., Helium

Column Temperature: 150°C
↓ (15°C/min)
275°C (5 min.)

Injector Temperature: 300°C

Lower Limit of Analysis: 25 ng injected, except n-nitrosodimethylamine - 50 ng injected

Suggested Alternative Methods

1. Alternative detectors are:
   - a. Alkali Flame Ionization Detector

AFID Temperature:	325°C
H_2 Flow:	3 mLs/min.
Air Flow:	50 mL/min.
GC/AFID Detection Limit:	1 ng injected, except p-nitrosodiphenylamine - 25 ng injected

   - b. Hall (electroconductivity) Detector
   - c. Electron Capture Detector

2. Other alternative columns include a 4% Carbowax 20M on Carbopack B + 0.8% KOH, 2m x 2mm glass column (see amine analysis); 10% Carbowax 20M + 2% KOH, Chromosorb WAW , 8m x 4mm[37], 10% SP 2250, 100/120 mesh Supelcoport, 1.8m x 4mm[37].

3. For non-volatile species, the following HPLC column can be used:
   - a. Porasil 30cm x 4mm, 5% acetone/95% isooctane, 2mL/min.
   - b. μBondapack C/18, 30cm x 4mm ID, 1.5% acetonitrite, 98.5% isooctane, 1.5 mL/min., detection is either by UV at 254 nm or with a thermal energy analyzer.

Reference

37. Federal Register, Volume 44, No. 233, December 3, 1979, pp. 69,496-69,500.

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NITROSAMINES - (MEG CATEGORY 12)

Method Evaluation

The analytical method originally recommended for the nitrosamines (MEG Category 12) in the Level 2 Sampling and Analysis Manual was:

Column:	3% SP 2100 on 100/120 Supelcoport, 3m x 2mm glass	
Conditions:	Flow Rate:	20 mL/min.
	Column Temperature:	90°C, isothermal

The recommended analytical finish for this category was evaluated using gas chromatography with alkali flame ionization detection (GC/AFID). The instrument used was a Hewlett Packard 5840A Gas Chromatograph. The recommended column, 3% SP 2100 on 100/120 Supelcoport, was conditioned overnight at 250°C.

A test mixture was prepared consisting of the compounds listed in Table 26 in methanol. Methanol was used as the solvent, rather than methylene chloride, because use of chlorinated solvents is not recommended with an AFID. The test mixture was chromatographed on the 3% SP 2100 GC column, using the recommended conditions, to determine whether the compounds were adequately resolved. The original method recommended a temperature program of 90°C isothermal; however, column temperature programming was found to be more appropriate for the test mixture. GC column temperature programming from 150°C to 275°C (isothermal, five minutes) at a program rate of 15°C per minute was experimentally determined to be adequate. The initial temperature could be lowered for analysis of lower-boiling nitrosamine compounds or, if necessary, to resolve n-nitrosodipropylamine from the methanol solvent GC peak for GC/MS analysis.

Methanol is not detected using AFID, because this detector is selective for nitrogen and phosphorous. Therefore, resolving n-nitrosodipropylamine from the methanol GC solvent peak is not necessary. However, it is desirable to resolve low boiling nitrosamine compounds from methanol when using GC/MS, to avoid introducing a large volume of solvent into the MS ion source. The solvent in the ion source would deplete the number of electrons available, thereby decreasing the ionizing efficiency.

The previous suggestion of a hydrogen flow of 6 mL/min. to the alkali flame ionization detector was changed to 3 mL/min. to conform to the recommendation of the AFID manufacturer (Hewlett Packard).

It was necessary to determine the GC peak retention time of each compound in the test mixture. This was done by chromatographing a solution of each compound. Retention times for each of the compounds in the test mixture are presented in Table 26. A representative gas chromatogram is presented in Figure 25.

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The lower limit of analysis for each nitrosamine compound was determined. Test mixtures, corresponding to concentrations of 25 ng/μL, 5 ng/μL, and 1 ng/μL were prepared in methanol. These test mixtures were chromatographed using the revised recommended conditions. Two of the compounds, n-nitrosodipropylamine and n-nitrosodiphenylamine, were analyzed at 1 ng injected on column. The third compound, p-nitrosodiphenylamine, could be analyzed only at 25 ng injected on column. Severe GC peak tailing prevented p-nitrosodiphenylamine from being analyzed at lower concentrations.

In another program[36,37] it was established that n-nitrosodiphenylamine decomposes to form diphenylamine at normal operating temperatures of the GC injector port, e.g., at temperatures as low as 145°C. Since n-nitrosodiphenylamine is being measured and detected as diphenylamine, preliminary clean-up steps must be followed to remove any diphenylamine from the original sample prior to GC analysis. EMSL, EPA[37] recommends that alumina or florisil be used to remove diphenylamine.

Evidence concerning the precision and accuracy of the GC/MS method of analyzing nitrosamine compounds is available from other programs[10,11]. In one study[10], a mixture of compounds including three nitrosamine compounds was added to clean water and raw wastewater to obtain a concentration level of 50 μg/L. One liter aliquots of the water, adjusted to a pH greater than 11, were extracted three times with methylene chloride (250 mL, 100 mL, 100 mL). The extracts were concentrated to 2 mL, and 2 μL of these extracts were then analyzed by GC/MS, using a 1% SP 2250 GC column. The observed detection limit (DL) for each nitrosoamine compound using GC/MS is listed below. Concentration values were calculated relative to an internal standard. The average recoveries ($\overline{P}$) and standard deviations (SP) of replicate analyses for the three compounds follows:

	Clean Water(a)		Raw Municipal(b) Wastewater		Limits of(c) Analysis
Compounds	$\overline{P}$	Sp	$\overline{P}$	Sp	
N-Nitrosodimethylamine	-	-	-	-	40 ng
Nitroso-di-n-propylamine	93	19	99	28	20 ng
N-Nitrosodiphenylamine	140	14	156	34	10 ng

(a) Based on 7 data points
(b) Based on 14 data points
(c) GC/MS limit of analysis - nanograms injected, based on the y-intercept of the calibration curve

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N-Nitrosodimethylamine (NDMA) has a higher limit of analysis (40 ng) than the other nitrosamine compounds, because the GC peak attributed to NDMA chromatographs poorly (excessive peak tailing) on the 1% SP 2250 GC column. Due to this high detection limit and a low percent recovery (approximately 50% from water[36]) for NDMA, the compound was not detected in the wastewater study. It is expected that when using the Level 2 revised recommended method with alkali flame ionization detection (AFID), the limit of analysis should be adequate to analyze NDMA at the DMEG concentration values (Air - 1.2 μg/m^3 and water - 18 μg/L) after sample preparation (e.g., XAD-2 extraction, liquid/liquid extraction). However, when using GC/MS techniques, the limit of analysis for NDMA may not be adequate even with improved chromatography on the 3% SP 2100 GC column. There is evidence[37] that NDMA chromatographs better on the suggested alternative column, 10% Carbowax 20M/2% KOH, Chromosorb WAW.

TABLE 26

Analytical Data for Nitrosamines

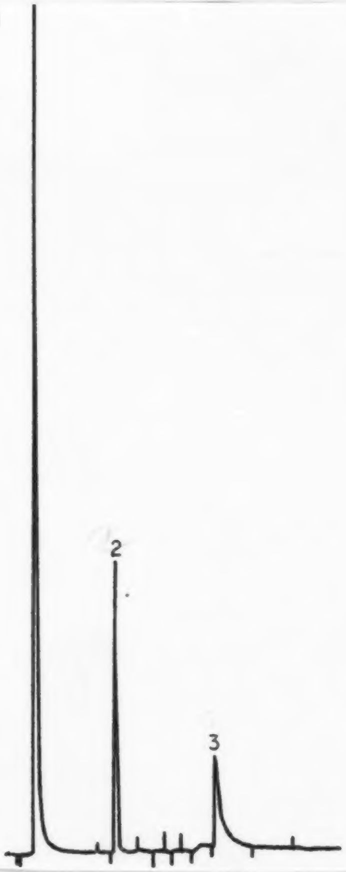
(MEG Category 12)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC(a) Peak No.	RRT(b)
12	N-nitrosodipropylamine	$(CH_3CH_2CH_2)_2$ NNO	130	206	1	0.27
12	N-nitrosodiphenylamine	(C_6H_4) NNO (C_6H_5)	198	solid	2	1.00
12	p-nitrosodiphenylamine	$NOC_6H_4NHC_6H_5$	198	solid	3	1.89

(a) Numbers refer to gas chromatogram, Figure 25.

(b) Relative retention time (relative to N-nitrosodiphenylamine, RT = 3.28 minutes)

Sample:	167 ng each nitrosamine in 1 μL methanol
Column:	3% SP 2100 on 100/120 mesh Supelcoport, 2m x 2mm glass
Carrier Gas:	20 mL/min., Helium
Column Temperature:	150°C $\xrightarrow{\text{15°C/min.}}$ 275°C (5 min.)
Injector Temperature:	290°C
AFID Detector Temperature:	325°C
AFID H Flow:	3 mL/min.
AFID Air Flow:	50 mL/min.
Attenuation:	2^{12}
Chart Speed:	0.5 cm/min.



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(GC peak numbers refer to Table 26)

Figure 25. Gas Chromatogram of Nitrosamines

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Mercaptans, Sulfides, and Disulfides (MEG Category 13)

The recommended analytical method for the mercaptans, sulfides, and disulfides (MEG Category 13) is gas chromatography/mass spectroscopy. This method has not been evaluated during this program.

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MERCAPTANS, SULFIDES, AND DISULFIDES (MEG CATEGORY 13)

Recommended Method

Recommended Method: GC/MS

A. Species with Boiling Points in the Range 6°C to 60°C

Due to the difficulty of storing species such as methyl mercaptan, these should be analyzed by on-site GC using the column specified by the Level 1 procedure.

B. Species with Boiling Points greater than 60°C

Column:	3% SP 1000 on 100/120 Supelcoport, 2m x 2mm glass column
Example Conditions:	Flow Rate: 20 mL/min.
	Column Temperature: 100°C → 6°C/min. → 200°C
Detection Limit:	50 ng injected

Suggested Alternative Methods

1. The following column has been used to separate low molecular weight compounds in this category:

   Column: Chromasil 300, 2m x 2mm Teflon
   Flow Rate: 20 mL/min.
   Temperature: 65°C (retention of N-butyl mercaptan = 8 min., methyl disulfide = 9 min.) (Reference 38)

2. Flame Photometric (Reference 39) or Flame Ionization Detection can be used for interference-free samples.

References

38. "Analysis of Sulfur Gases," Supelco Bulletin 722F, Supelco, Inc., Bellefonte, PA.

39. Stevens, R.K., and A.E. O'Keefe, Analytical Chemistry, 42, 142-A (1970).

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Sulfonic Acids and Sulfoxides (MEG Categories 14A and 14B)

The analytical method recommended by sulfonic acids (MEG Category 14A) is a reverse-phase ion-pair/high performance liquid chromatography procedure. The analytical method recommended for sulfoxides (MEG Category 14B) is gas chromatography/mass spectroscopy.

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SULFONIC ACIDS AND SULFOXIDES (MEG CATEGORIES 14A and B)

Recommended Method

A. Sulfonic Acids

Recommended Method: Reverse-phase ion-pair liquid partition chromatography (Reference 40)

Column: LiChrosorb SI 60 silanized or Bondapak C18/Porasil B coated with 10% tri-n-octylamine; 195 to 300mm x 3mm ID

Mobile Phase: Tetrabutyl-ammonium in aqueous phosphate buffer, pH 7.4; or aqueous perchloric acid in pH ~2.6. Maintained at 25°C; eluted at 0.7 - 2.5mm/sec.

Detector: UV at 254 nm

Lower Limit of Analysis: 10 to 50 ng injected

B. Sulfoxides

Recommended Method: GC/MS

Column: 3% SP 1000 on 100/120 mesh Supelcoport, 2m x 2mm glass column

Example Conditions: Flow Rate: 30 mL/min.
Column Temperature: Isothermal 165°C

Lower Limit of Analysis: ~50 ng injected (each component)

Suggested Alternative Methods

1. The following reverse-phase ion-pair high performance liquid chromatography technique was developed (Reference 41) for the analysis of linear alkyl benzene sulfonates.

   Column: Perkin-Elmer HC-ODS Sil-X, 5 micron

   Example Conditions:

   Mobile Phase: 0.015M tetramethylammonium chloride in 80/20 MeOH-H_2O, pH 2.8 (adjusted with H_2SO_4)

   Flow Rate: 1.0 mL min^{-1}

   Injector Volume: 30 μL

   Detector: UV λ222 nm

   Attenuation: X0.02AUFS

Note: This procedure may be modified to resolve each of the linear alkyl benzene sulfonates.

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References

40. Kraak, J.C., and J.F.K. Huber, *J. Chromatography*, 102 (1974), 333-351, Wahlund, K.G. *ibid.* 115 (1975) 411-422.

41. Arthur D. Little, Inc., "Development of an Analytical Method for Linear Alkyl Benzene Sulfonates in Cows' Milk", Report to Economics Laboratories, Inc., 8/26/80.

SULFONIC ACIDS AND SULFOXIDES (MEG CATEGORIES 14A and B)

The recommended alternative method for sulfonic acids and sulfoxides (Alternative No. 1) is a high performance liquid chromatography (HPLC) procedure[41]. This procedure was designed to measure the linear alkyl benzene sulfonates as an unresolved group of HPLC peaks. This procedure may be modified to resolve each of the linear alkyl benzene sulfonates. A representative HPLC chromatogram is presented in Figure 26.

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Sample:	10.2 ppm LAS in 30 μL MeOH
Column:	Perkin Elmer HCODS, Sil-x, 5 μL, 25cm x 4.6mm
Solvent:	CH_3OH/H_2O (80:20), tetramethylammonium chloride (1.65 g/L), pH 2.8 (with H_2SO_4)
Flow Rate:	1 mL/min.
UV Detector:	222 nm
Attenuation x Range:	0.02 AUFS
Chart Rate:	0.21 in/min., 10 mV

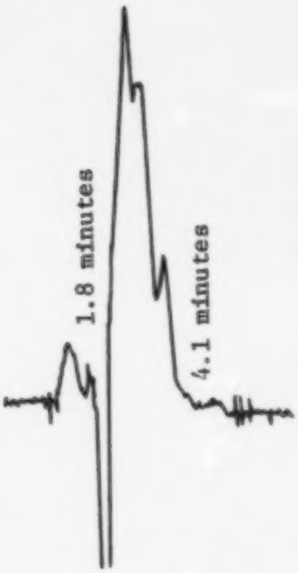

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Figure 26. HPLC Chromatogram of Linear Dodecyl Benzene Sulfonates

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Benzene and Substituted Benzene Hydrocarbons (MEG Category 15)

The analytical method recommended for the benzene and substituted benzene hydrocarbons (MEG Category 15) is gas chromatography/mass spectroscopy. Two GC columns are recommended for this category, based on boiling point ranges. These boiling point ranges overlap, thus offering flexibility when choosing a GC column for a Level 2 analysis.

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BENZENE AND SUBSTITUTED BENZENE HYDROCARBONS - (MEG CATEGORY 15)

Recommended Method

A. Species with Boiling Points in the Range 80°C to 200°C

Column: 0.1% SP 1000 on 80/100 mesh Carbopack C
2m x 2mm glass on stainless steel (Reference 42)

Example Conditions: Carrier Gas: 20 mL/min. Helium

Column Temperature: 110°C
↓ 15°C/min.
220°C (7 min.)

Lower Limit of Analysis: 5 ng injected

B. Species with Boiling Points greater than 110°C

Column: 3% SP 2250 on 100/120 mesh Supelcoport
2mm x 2m glass column (Reference 42)

Example Conditions: Carrier Gas: 20 mL/min. Helium

Column Temperature: 60°C (5 min.)
↓ 10°C/min
250°C (3 min.)

Injector Temperature: 275°C

Lower Limit of Analysis: 10 ng injected

Suggested Alternative Methods

1. GC/FID (same chromatographic conditions as above) is an alternative detection system for preliminary evaluation or for interference-free samples.

   a. Species with Boiling Points in the Range 80°C to 200°C

      FI Detector Temperature: 270°C
      Lower Limit of Analysis: 2 ng injected on column

   b. Species with Boiling Points greater than 110°C

      FI Detector Temperature: 300°C
      Lower Limit of Analysis 10 ng injected

2. Alternate GC columns for low boiling aromatics are:

   a. 0.2% Carbowax 1500/Carbopack C, 60/80, 2m x 2mm glass or stainless steel (typically used with samples prepared by purge-and-trap);

      Example Conditions: Flow Rate: 20 mL/min.

      Column Temperature: 60°C (3 min.)
      ↓ 8°C/min.
      160°C

      Retention of ethylbenzene is 20 min. (References 43,44)

References

42. "Separation of Hydrocarbons," Supelco Bulletin 743B, Supelco, Inc., Bellefonte, PA.

43. "Carbopack," Supelco Bulletin 738B, Supelco, Inc., Bellefonte, PA.

44. "Water Pollution Analysis and Standards," Supelco Bulletin 775, Supelco, Inc., Bellefonte, PA.

BENZENE AND SUBSTITUED BENZENE HYDROCARBONS - (MEG CATEGORY 15)

Method Evaluation

A. Species with Boiling Points in the Range of 80°C to 200°C

The analytical method originally recommended for benzene and substituted benzene hydrocarbons with boiling points in the range of 80°C to 200°C in the Level 2 Sampling and Analysis Manual was:

Column:	0.1% SP 1000 on 80/100 mesh Carbopack C, 2m x 2mm glass on stainless steel	
Example Conditions:	Flow Rate:	20 mL/min.
	Column Temperature:	Isothermal at 225°C

The recommended analytical finish for this category was evaluated using gas chromatography with flame ionization detection (GC/FID). The instrument used was a Hewlett Packard 5840A Gas Chromatograph. The recommended GC column, 0.1% SP 1000 on 80/100 mesh Carbopack C, was conditioned for four hours at 220°C.

A test mixture was prepared consisting of the benzene compounds listed in Table 27 in methylene chloride. This test mixture was chromatographed on the 0.1% SP 1000 GC column, using the recommended conditions to determine whether the compounds were adequately resolved. It was necessary to use sample injection volumes ≤0.5 µL to avoid plugging the column. The original method recommended a GC column temperature of 225°C isothermal, however, GC column temperature programming is more appropriate for the test mixture.

The GC temperature programming from 110°C to 220°C (isothermal 7 minutes) at 15°C per minute was experimentally determined to be adequate. Benzene may be collected in a gas sample (in glass bulbs) or in an aqueous sample. Aqueous samples containing benzene may be prepared by liquid/liquid extraction or purge and trap techniques. It is most important to resolve benzene from methylene chloride when extracting with methylene chloride. It is not as important when the sample is being analyzed as a gas or when using the purge and trap technique.

It was necessary to determine the GC peak retention times of each benzene compound in the test mixture. These were determined by chromatographing a solution of each compound. Retention times for each of the compounds in the test mixture are presented in Table 27. A representative gas chromatogram is presented in Figure 27.

The lower limit of analysis for each benzene compound was determined. A test mixture in methylene chloride, corresponding to a concentration of 2.5 ng per 0.5 μL injection, was prepared. This test mixture was chromatographed using the revised recommended conditions. Each compound was easily analyzed at 2.5 ng injected on column.

Evidence concerning the precision and accuracy of the GC/MS method for analysis of benzene compounds may be inferred from results obtained in other programs. In one study[10], a mixture of compounds including three benzene compounds was added to clean water and to raw municipal wastewater to obtain a concentration level of 20 μg/L. Five milliliter aliquots of the water samples were purged with helium gas to transfer volatile species onto a Tenax/Silica Gel trap. The trap was subsequently backflushed onto a 0.2% Carbowax 1500/Carbopack C GC column, and analyzed using GC/MS. In that analysis, the observed limit of analysis for each benzene compound was 1 μg/L. Concentration values were calculated relative to an internal standard using a standard curve. The average recoveries ($\overline{P}$) and standard deviations (Sp) of replicate analyses for the three compounds follow.

Compound	Clean Water(a)		Raw Municipal Wastewater(b)	
	$\overline{P}$	Sp	$\overline{P}$	Sp
Benzene	88	7	90	11
Toluene	99	31	96	31
Ethylbenzene	122	21	122	32

(a) Based on 15 data points

(b) Based on 30 data points

TABLE 27

Analytical Data for Benzene and Substituted Benzene Hydrocarbons with Boiling Points in the Range 80°C to 200°C

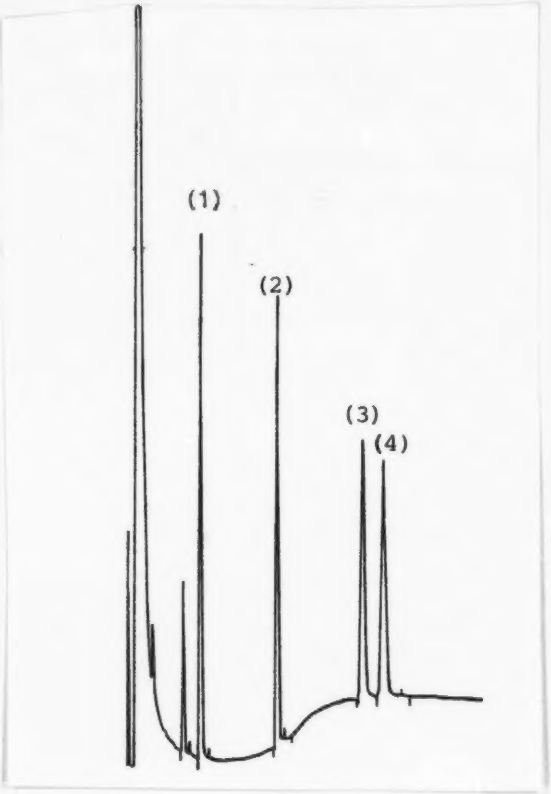
(MEG Category 15)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC(a) Peak No.	RRT(b)
15	Benzene	C_6H_6	78	80	1	0.34
15	Toluene	C_7H_8	92	111	2	0.65
15	Styrene	C_8H_8	104	145	3	1.00
15	t-Butylbenzene	$C_{10}H_{14}$	134	169	4	1.08

(a) Numbers refer to gas chromatogram, Figure 27.

(b) Relative Retention Times (relative to styrene RT = 9.67 minutes)

Sample:	62.5 nanograms of each compound in 0.5 μL methylene chloride
Column:	0.1% SP 1000 on 80/100 mesh Carbopack C, 2m x 2mm glass
Carrier Gas:	20 mL/min., Helium
Column Temperatur	110°C $\xrightarrow{15°C/min.}$ 220°C (7 min.)
Injector Temperature:	250°C
FI Detector Temperature:	270°C
Attenuation:	2^7
Chart Speed:	0.5 cm/min.



(GC peak numbers refer to Table 27)

Figure 27. Gas Chromatogram of Benzene and Substituted Benzene Hydrocarbons (with Boiling Points in the Range 80°C to 200°C)

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B. Species with Boiling Points greater than 110°C

The analytical method originally recommended for benzenes and substituted benzene hydrocarbons with boiling points greater than 110°C in the Level 2 Sampling and Analysis Manual was:

Column:	3% SP 2250 or equivalent on 100/120 mesh Supelcoport, 2m x 2mm glass or stainless steel
Example Conditions:	Carrier Gas: 20 mL/min., Helium
	Column Temperature: $70°C \xrightarrow{10°C/min.} 300°C$

The recommended analytical finish for this category was evaluated using gas chromatography with flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph. The recommended GC column, 3% SP 2250 on 100/120 mesh Supelcoport, was conditioned overnight at 250°C.

A test mixture was prepared consisting of the compounds listed in Table 28 in methylene chloride. This test mixture was chromatographed on the 3% SP 2250 column, using the recommended conditions, to determine whether the individual compounds were adequately resolved. The original method recommended a temperature program of 70°C $\xrightarrow{10°C/min.}$ 300°C. This was changed to a temperature program of 60°C (isothermal, 5 minutes) $\xrightarrow{10°C/min.}$ 250°C (isothermal, 3 minutes). Because of poor resolution of the low boiling benzene compounds, m-xylene, o-xylene, and styrene, from the solvent GC peak, the initial temperature was changed to 60°C. The final temperature was lowered to 250°C, because that temperature with the three-minute hold was sufficient to elute terphenyl, the highest boiling compound in the test mixture.

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It was necessary to determine the GC peak retention times of each benzene compound in the test mixture. The retention times were determined by sequentially adding each of the compounds to methylene chloride and chromatographing the solution after each addition. Retention times for each of the compounds in the test mixture are presented in Table 28. A representative gas chromatogram is presented in Figure 28.

The detection limits for each benzene compound were determined. Three test mixtures in methylene chloride, corresponding to concentrations of 60 ng/μL, 30 ng/μL, and 10 ng/μL, were prepared. These test mixtures were chromatographed using the revised recommended conditions. Each of the compounds was readily detected at 10 nanograms injected on the column. Slight modifications of the GC temperature program, however, would improve resolution of the early eluting compounds, m-xylene, o-xylene, and styrene, from the solvent GC peak and consequently improve the detection limit even further.

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TABLE 28

Analytical Data for Benzene and Substituted Benzene Hydrocarbons with Boiling Points greater than 110°C

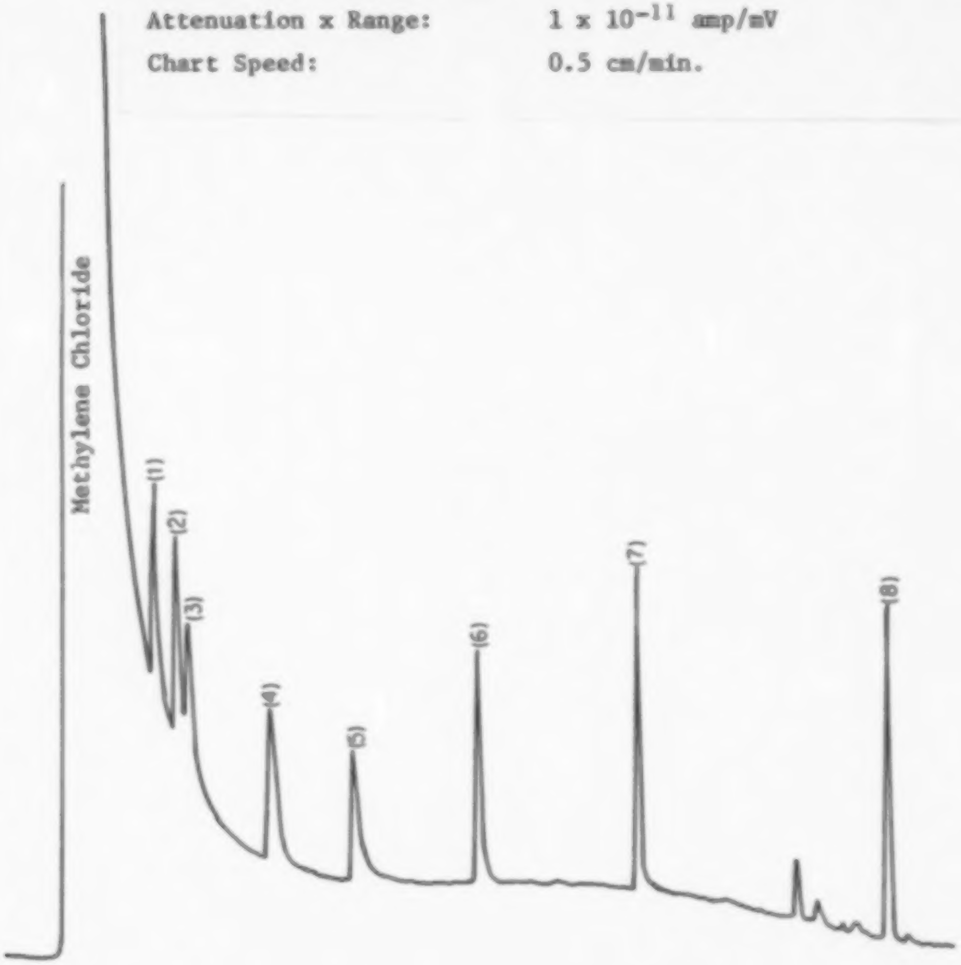
(MEG Category 15)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC Peak No.(a)	RRT(b)
15	m-xylene	C_8H_{10}	106	144	2	.30
15	o-xylene	C_8H_{10}	106	139	1	.24
15	styrene	C_8H_8	104	145	3	.32
15	t-butylbenzene	$C_{10}H_{14}$	134	169	4	.52
15	n-butylbenzene	$C_{10}H_{14}$	134	183	5	.71
15	1,2,3,4-tetrahydro-naphthalene	$C_{10}H_{12}$	132	207	6	1.00
15	biphenyl	$C_{12}H_{10}$	154	255	7	1.37
15	O-terphenyl	$C_{18}H_{14}$	230	332	8	1.95

(a) Numbers refer to gas chromatogram, Figure 28.

(b) Relative Retention Times (relative to 1,2,3,4-tetrahydronaphthalene, RT = 12.8 min.)

Sample:	30 nanograms of each compound in 1 µL methylene chloride
Column:	3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm glass
Carrier Gas:	20 mL/min., Helium
Column Temperature:	60°C (5 min.) $\xrightarrow{10°C/min}$ 250°C (3 min.)
Injector Temperature:	270°C
FI Detector Temperature:	300°C
Attenuation x Range:	1 x 10^{-11} amp/mV
Chart Speed:	0.5 cm/min.



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(GC peak numbers refer to Table 28)

Figure 28. Gas Chromatogram of Benzene and Substituted Benzene Hydrocarbons

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Halogenated Aromatic Compounds (MEG Category 16)

The analytical method recommended for halogenated aromatic compounds (MEG Category 16) is gas chromatography/mass spectroscopy. This category includes halogen ring substituted aromatics and halogenated alkyl side chain substituted aromatics.

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HALOGENATED AROMATIC COMPOUNDS --MEG CATEGORY 16

Recommended Method

Recommended Method: GC/MS

Column: 3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm stainless steel or glass

Example Conditions: Carrier Gas: 30 mL/min., Helium

Column Temperature: 75°C

↓ 8°C/min.

260°C (15 min.)

Lower Limit of Analysis: 10 ng injected

Suggested Alternative Methods

1. GC/ECD is an alternative detection system for preliminary evaluation or for interference-free samples.

   Column: 3% SP 2250

   Example Conditions: Column Temperature: 110°C (compounds with boiling points less than 250°C).

   GC/ECD Detection Limits: 50 pg to 25 ng (depending on degree of halogenation)

HALOGENATED AROMATIC COMPOUNDS - (MEG CATEGORY 16)

Method Evaluation

The analytical method originally reccommended for the halogenated aromatic compounds (MEG Category 16) in the Level 2 Sampling and Analysis Manual was:

Recommended Method: GC/MS

Column: 3% SP 2250 on 100/120 mesh Supelcoport,
2m x 2mm glass or stainless steel

Example Conditions: Flow Rate: 30 mL/min.

Column
Temperature: 75°C
↓ 8°C/min.
260°C (15 min.)

Detection Limit: 10 ng injected

The analytical finish for the halogenated aromatic compounds was evaluated using gas chromatography/electron capture detection (GC/ECD). The instrument used was a Hewlett-Packard 5840 Gas Chromatograph. The GC column, 3% SP 2250 on 80/100 mesh Supelcoport, was conditioned overnight at 350°C.

Two test mixtures were prepared consisting of the compounds listed in Table 29 and Table 31 in hexane. Hexane was chosen as the solvent in this analysis because of its low response characteristics for GC/ECD analysis. The previously recommended program could not be used since the electron capture detector was found to be stable only for isothermal operation. The compounds listed in Table 29, which have boiling points less than 250°C, were chromatographed at 110°C isothermally, while those compounds listed in Table 31, which have boiling points greater than 250°C, were chromatographed at 160°C isothermally. The division of the halogenated aromatic compounds into two categories was necessary in order to reduce both peak broadening and analysis time.

Two test mixtures were chromatographed on the 3% SP 2250 GC column at 110°C and 160°C isothermally to determine whether the individual compounds were adequately resolved. The individual components of the test mixtures were identified by sequentially adding each of the halogenated aromatic compounds to hexane and chromatographing the solution after each addition.

The retention times of the halogenated aromatic GC peaks are given in Tables 29 and 31, and the representative gas chromatograms are presented in Figures 29 and 30. The GC peaks attributable to 4-bromochlorobenzene and α-bromotoluene were not resolved. In GC/MS analysis, appropriate ions could be monitored by mass spectroscopy to distinguish the two compounds.

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The lower limit of analysis for each halogenated aromatic compound was then determined. A stock test mixture was prepared for each of the two boiling point groups of the halogenated aromatic compounds. The stock mixtures and three dilutions of each stock test mixture (1:4, 1:10, 1:20) were chromatographed at the appropriate temperatures. The concentrations of each halogenated aromatic compound in the stock mixture and its dilutions are listed in Tables 30 and 32, corresponding to compounds with boiling points less than 250°C and greater than 250°C, respectively. The concentrations of the individual halogenated aromatic compounds were varied to compensate for the wide range of differences in sensitivity of the electron capture detector for compounds with different degrees of halogenation. The individual halogenated aromatic compounds in the test mixtures were easily detected using ECD at the lowest concentration tested, which ranged from 50 picograms for 1,2,4-trichlorobenzene to 25 ng for 4,4′-dichlorobiphenyl.

Evidence concerning the precision and accuracy of this method of analyzing halogenated aromatics is available from other programs. In one study[10], a mixture of compounds, including six halogenated aromatic compounds, was added into deionized, distilled, organic-free water and to raw municipal wastewater to give a concentration level of 50 μg/L. One liter aliquots of the water samples, adjusted to a pH greater than 11, were extracted three times with methylene chloride (250 mL, 100 mL, 100 mL). These extracts were then analyzed by GC/MS, using a 3% SP 2250 DB GC column. The observed detection limit for each halogenated aromatic compound using GC/MS was 10 ng injected, relative to an internal standard. The average recoveries ($\bar{P}$) and standard deviations (Sp) of replicate analyses for the six compounds were as follows:

Compound	Clean Water(a)		Raw Municipal Wastewater(b)	
	$\bar{P}$	Sp	$\bar{P}$	Sp
1,3-Dichlorobenzene 1,4-Dichlorobenzene 1,2-Dichlorobenzene	64	19	58	13
1,2,4-Trichlorobenzene	75	14	82	14
2-Chlorobenzene	86	18	81	19
Hexachlorobenzene	80	11	63	16

(a) Based on 7 data points

(b) Based on 14 data points

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In the same program[10], PCB 1254 was added into clean water and raw municipal wastewater. One liter aliquots of the water samples were extracted three times with 15% methylene chloride/85% hexane (60 mL, 60 mL, 60 mL) and chromatographed on Florisil. These extracts were analyzed by GC/ECD, using a 1.5% SP 2250/1.95% SP 2401 column. The observed detection limit for the PCBs using GC/ECD was approximately 500 picograms injected. The average recoveries ($\overline{P}$) and standard deviations (Sp) of replicate analyses relative to an internal standard for an Arochlor standard were:

Compound	Clean Water[(a)]		Raw Municipal Wastewater[(b)]	
	$\overline{P}$	Sp	$\overline{P}$	Sp
PCB 1254	89	12	83	14

In another program[9], microextraction was used to prepare aqueous samples for GC/ECD analysis of halogenated aromatics. In this study, a mixture of compounds including fourteen halogenated aromatics was added to deionized, distilled, organic-free water to give concentration levels between 42 μg/L and 126 μg/L. Sixty grams of NaCl were added to 180 mL aliquots of the water samples and subsequently extracted with 2 mL hexane. These extracts were diluted and analyzed by GC/ECD, using a 3% SP 2250 GC column. The average recoveries and standard deviations of replicate analyses for the fourteen compounds were as follows:

Compound	Average Recovery*	S.andard Deviation*
m-Cl_2-Benzene	87	3.7
p-Cl_2-Benzene	93	6.8
o-Cl_2-Benzene		
2,4-Cl_2-Toluene	84	4.0
3,5-Cl_2-Toluene		
2,6-Cl_2-Toluene		
2,5-Cl_2-Toluene		
1,3,5-Cl_3-Benzene	102	7.7
2,3-Cl_2-Toluene		
3,4-Cl_2-Toluene	88	6.5
1,2,4-Cl_3-Benzene	95	5.3
1,2,3-Cl_3-Benzene	94	6.97
1,2,4,5-Cl_4-Benzene	96	5.3
1,2,3,4-Cl_4-Benzene		

*Based on 5 data points.

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TABLE 29

Analytical Data for Halogenated Aromatics with Boiling Points less than 250°C

(MEG Category 16)

MEG Category No.	Compound	Composition	MW	BP (°C)	GC[(a)] Peak No.	RRt[(b)]
16	1,3-Dichlorobenzene	$C_6H_4Cl_2$	147	173	1	.39
16	4-Bromochlorobenzene	C_6H_4BrCl	191	196	2	.69
16	α-Bromotoluene	$C_6H_5CH_2Br$	171	201	2	.69
16	1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	181	214	3	1.00
16	1,2-Dibromobenzene	$C_6H_4Br_2$	236	225	4	1.43

(a) Numbers refer to gas chromatogram, Figure 29.

(b) Relative Retention Times (relative to 1,2,4-trichlorobenzene, RT = 3.64 min.)

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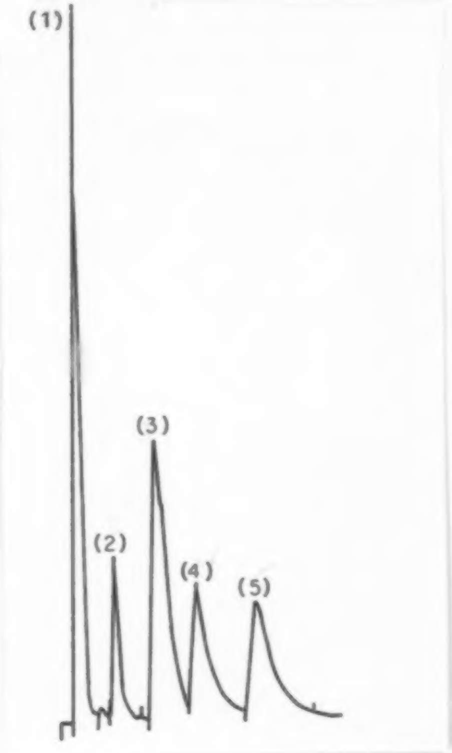
Sample:	300 ng - 1,3 dichlorobenzene, 50 ng - 4-bromochlorobenzene, 20 ng - bromotoluene 1.0 ng - 1,2,4-trichlorobenzene, 1.0 ng - 1,2-dibromobenzene in 1.0 μL hexane
Column:	3% SP 2250, 100/120 Supelcoport, 2m x 2mm glass
Column Temperature:	110°C
ECD Temperature:	250°C
Injector Temperature:	225°C
Attenuation:	2 ↑ 10
Carrier Gas:	20 mL/min., 95% Argon/5% Methane
Chart Speed:	0.75 cm/min.



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(GC peak numbers refer to Table 29)

Figure 29. Gas Chromatogram of Halogenated Aromatic Compounds with Boiling Points less than 250°C

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TABLE 30

Concentrations of Halogenated Aromatics with Boiling Points less than 250°C

(MEG Category 16)

Compound	Stock ng/μL	1 to 4 Dilution ng/μL	1 to 10 Dilution ng/μL	1 to 20 Dilution ng/μL
1,3-Dichlorobenzene	300	75	30	15
4-Bromochlorobenzene	50	12.5	5.0	2.5
α-Bromotoluene	20	5.0	2.0	1.0
1,2,4-Trichlorobenzene	1.0	0.25	0.10	0.05
1,2-Dibromobenzene	1.0	0.25	0.10	0.05

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TABLE 31

Analytical Data for Halogenated Aromatics with Boiling Points greater than 250°C

(MEG Category 16)

MEG Category No.	Compound	Composition	MW	BP (°C)	GC[a] Peak No.	RRT[b]
16	4,4'-Dichlorobiphenyl	$C_{12}H_8Cl_2$	223	315-9	1	.48
16	1,3,5-Tribromobenzene	$C_6H_3Br_3$	315	271	2	1.00

(a) Numbers refer to gas chromatogram, Figure 30.

(b) Relative Retention Times (relative to 1,3,5-tribromobenzene, RT = 2.83 min.)

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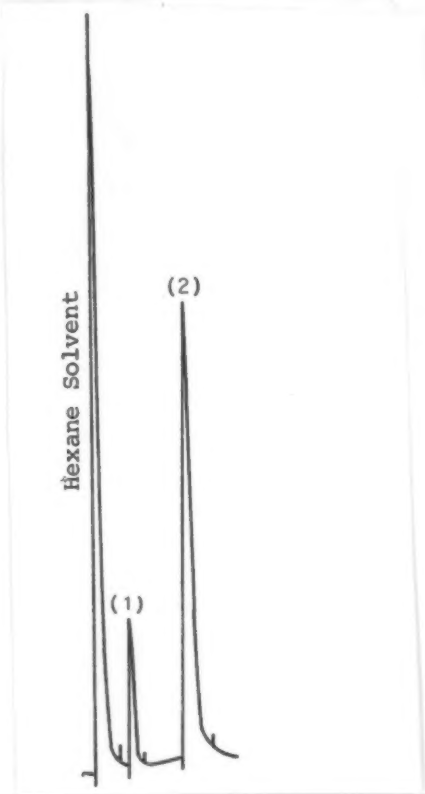
Sample:	500 ng - 4,4'-dichlorobiphenyl, 2.5 ng - 1,3,5-tribromobenzene in 1.0 μL hexane
Column:	3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm glass
Column Temperature:	160°C, isothermal
ECD Temperature:	120°C
Injector Temperature:	225°C
Carrier Gas:	20 mL/min., 95% Argon/5% Methane
Chart Speed:	0.75 cm/min.
Attenuation:	2 ↑ 8



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(GC peak numbers refer to Table 31)

Figure 30. Gas Chromatogram of Halogenated Aromatic Compounds with Boiling Points greater than 250°C

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TABLE 32

Concentrations of Individual Halogenated Aromatics with Boiling Points greater than 250°C

(MEG Category 16)

Compound	Stock ng/μL	1 to 4 Dilution ng/μL	1 to 10 Dilution ng/μL	1 to 20 Dilution ng/μL
4,4′-Dichlorbiphenyl	500	125	50	25
1,3,5-Tribromobenzene	2.5	0.625	0.25	0.125

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Aromatic Nitro Compounds (MEG Category 17)

The analytical method recommended for aromatic nitro compounds (MEG Category 17) is gas chromatography/mass spectroscopy.

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AROMATIC NITRO COMPOUNDS - (DMEG CATEGORY 17)

Recommended Method

Recommended Method: GC/MS

Column: 3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm glass column

Example Conditions: Carrier Gas: 30 mL/min., Helium

Column Temperature: 60°C
↓ 8°C/min.
230°C

(Reference 45)

Injector: 300°C

Lower Limit of Analysis: 10 ng injected

Suggested Alternative Methods

1. GC/FID or ECD is an alternative detection system for preliminary evaluation or for interference-free samples.

   Flame Ionization Detector: 325°C

   GC/FID Lower Limit of Analysis: 10 to 25 ng injected

2. An alternative GC column is 1.5% SP 2250 + 1.95% SP 2401 on 100/120 mesh Supelcoport, 2mm x 2m glass column

   Column Temperature: 80°C
   ↓ 8°C/min.
   300°C

   (Reference 46)

References

45. Goerlitz, D., L.M. Law, "GC Method for the Analysis of TNT and RDX Explosives Contaminating Water and Soil Core Material," U.S. Department of the Interior, Geological Survey, Water Resources Division, Report 75-182 (1975).

46. Federal Register, Volume 44, No. 233, Monday December 3, 1979, pp. 69510 - 69512.

AROMATIC NITRO COMPOUNDS - (MEG CATEGORY 17)

Method Evaluation

The analytical method originally recommended for aromatic nitro compounds (MEG Category 17) in the Level 2 Sampling and Analysis Manual was:

Column:	3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm glass or stainless steel
Example Conditions:	Flow Rate: 30 mL/min.
	Column Temperature: 100°C
	↓ 10°C/min.
	350°C

The analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph. The recommended GC column, 3% SP 2250 on 100/120 mesh Supelcoport was conditioned overnight at 350°C. A test mixture was prepared consisting of the compounds listed in Table 33 in methylene chloride.

The test mixture was chromatographed on the 3% SP 2250 GC column, using the recommended conditions, to determine whether the individual compounds were adequately resolved.

The original method recommeded that the column be temperature programmed from 100°C to 350°C at 10°C per minute; this was changed to programming from 60°C to 230°C at 8°C per minute. This change was made to resolve the methylene chloride GC peak from the aromatic nitro compounds, and to resolve 1-chloro-4-nitrobenzene and 1-chloro-2-nitrobenzene. A representative gas chromatogram is presented in Figure 31.

It was necessary to determine the retention times of each aromatic nitro compound in the test mixture. The retention times were determined by sequentially adding each of the aromatic nitro compounds to methylene chloride, and chromatographing the solution after each addition.

The detection limit for each aromatic nitro compound was then determined. Three test mixtures in methylene chloride, corresponding to 100 ng/μL, 25 ng/μL and 10 ng/μL of each aromatic nitro compound were chromatographed using the revised recommended conditions.

The individual aromatic nitro compounds in the test mixture were easily detected using FID at 10 ng injected on the column, except that 1-chloro-4-nitrobenzene appeared as an unresolved shoulder on the 1-chloro-2-nitrobenzene GC peak at this level. It will be necessary to develop alternative GC conditions if these two compounds need to be analyzed separately. They cannot be resolved using the mass spectrometer, since their mass spectra are too simiiar to differentiate.

Evidence concerning the precision and accuracy of this method of analyzing nitro aromatic compounds is available from another program[10]. In that study, a mixture of compounds including three nitro aromatic compounds, was added into raw municipal wastewater to give a concentration level of 50 µg/L. One liter aliquots of the water samples, adjusted to a pH greater than 11, were extracted three times with methylene chloride (250 mL, 100 mL, 100 mL). These extracts were then analyzed by GC/MS using a 1% SP 2250 GC column. The observed detection limit for each nitro aromatic compound using GC/MS was 10 ng injected. The average recoveries ($\overline{P}$) from water and the range of relative standard deviations (Sp) of replicate analyses relative to an internal standard for the three compounds follow:

	Raw Municipal Wastewater	
Compound	$\overline{P}$	Range of Relative Standard Deviation
Nitrobenzene	78	10-28
2,6-Dinitrotoluene	86	20-25
2,4-Dinitrotoluene	62	19-43

These data were accumulated over a period of two years.

TABLE 33

Analytical Data for Aromatic Nitro Compounds

(MEG Category 17)

MEG Category No.	Compound	Composition	MW	BP °C	GC[(a)] Peak No.	RRt[(b)]
17	Nitrobenzene	$C_6H_5NO_2$	123	210	1	.69
17	1-Chloro-4-nitrobenzene	$C_6H_4ClNO_2$	158	242	2	.91
17	1-Chloro-2-nitrobenzene	$C_6H_4ClNO_2$	158	246	3	.93
17	5-Chloro-2-nitrotoluene	$C_7H_6ClNO_2$	172	Solid	4	1.00
17	1,4-Dichloro-2-nitrobenzene	$C_6H_3Cl_2NO_2$	192	267	5	1.07
17	2,6-Dinitrotoluene	$C_7H_6N_2O_4$	182	Solid	6	1.26
17	2,4-Dinitrotoluene	$C_7H_6N_2O_4$	182	300	7	1.3

(a) Numbers refer to Gas Chromatogram, Figure 31.

(b) Relative retention times (relative to 5-chloro-2-nitrotoluene), RT = 14.8 min.

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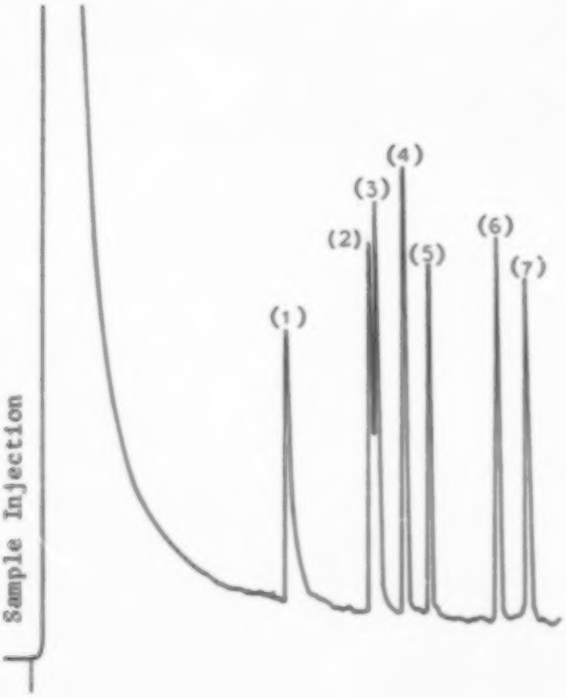
Sample:	~100 nanograms of each aromatic nitro compound in 1 μL CH_2Cl_2
Column:	3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm glass
Column Temperature:	60°C $\xrightarrow{8°C/min.}$ 230°C
Injector Temperature:	300°C
FI Detector Temperature:	325°C
Attenuation x Range:	2 x 10^{-11} amp/mV
Chart Speed:	0.5 cm/min.



(GC peak numbers refer to Table 33)

Figure 31. Gas Chromatogram of Aromatic Nitro Compounds

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Phenols, Halophenols, and Nitrophenols (MEG Categories 18, 19, 20)

The analytical method recommended for phenols, halophenols, and nitrophenols (MEG Categories 18, 19, 20) is gas chromatography/mass spectroscopy.

The compounds included in the phenol category (MEG 18) are divided into three subcategories:

Monohydrics (18A)
Dihydrics, Polyhydrics (18B)
Fused Ring Hydroxy Compounds (18C)

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PHENOLS, HALOPHENOLS, AND NITROPHENOLS - (MEG CATEGORIES 18, 19, 20)

Recommended Method

Recommended Method: GC/MS

Column: 1% SP 1240 DA on 100/120 mesh Supelcoport, 2m x 2mm glass column

Example Conditions: Carrier Gas: 30 mL/min., Helium

Column Temperature: 85°C (4 min.)

$$\big\downarrow \; 10°C/min.$$

200°C (15 min.) (Reference 47)

Injector: 200°C

Lower Limit of Analysis: 10 ng injected, except 2,4-dinitrophenol, 4,6-dinitro-2-cresol, and 4-nitrophenol - 25 ng injected

Suggested Alternative Methods

1. GC/FID (same chromatographic conditions as above) is an alternative detection system for interference-free samples.

   Detection Limit: 1-10 ng injected, except 4-nitrophenol and 4,6-dinitro-2-cresol - 25 ng injected

2. For polyhydric phenols and non-volatile phenols (e.g., hydroxy-BaP) and/or direct analysis of phenols in aqueous samples:

   HPLC, Reverse-Phase:

   Column: μBondapak/C18, 4mm x 300mm

   Mobile Phase: Water:Ethanol 60:40, 40 mL/hr.

   Detector: UV at 254 nm (Fluorescence at λEX 278 nm and λEM 320 nm has been used to analyze phenol) (References 9,48)

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References

9. Arthur D. Little, Inc. - Unpublished Data.

47. Federal Register, Volume 44, No. 233, Monday, December 3, 1979, pp. 69484 - 69488.

48. Edholm, L.E., and K. Callmer, "Liquid Chromatographic Study of Brominated Alkyl Phenols and Investigation of Product Formation in the Coulometric Bromination of Some Alkyl-Substituted Phenols," J. of Chrom., 137 (1977) 363-380.

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PHENOLS, HALOPHENOLS, AND NITROPHENOLS - (MEG CATEGORIES 19, 20, 21)

Method Evaluation

The analytical method originally recommended for phenols, nitrophenols, and halophenols (MEG Categories 18, 19, 20) in the Level 2 Sampling and Analysis Manual was:

Column:	1% SP 1240 DA on 100/120 mesh Supelcoport, 2m x 2mm glass column	
Example Conditions:	Carrier Gas:	30 mL/min.
	Column Temperature:	85°C ↓ 10°C/min. 200°C
Detection Limit:	50 ng injected	

The analytical finish for the three phenol MEG Categories was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Varian 2700 Gas Chromatograph.

The recommended GC column, 1% SP 1240 DA on 100/120 mesh Supelcoport, was conditioned overnight at 200°C. A test mixture was prepared consisting of the compounds listed in Table 34 in methylene chloride.

The test mixture was chromatographed on a 1% SP 1240 DA GC column, using the recommended conditions, to determine if the individual compounds were adequately resolved.

The only modification of the originally recommended method was to hold the upper column temperature for 15 minutes to elute 4-nitrophenol. A representative gas chromatogram is presented in Figure 32.

It was necessary to determine the retention times of each phenol in the test mixture. The retention times were identified by sequentially adding each of the phenol compounds to methylene chloride, and chromatographing the solution after each addition. The detection limit for each phenol was then determined. Five test mixtures in methylene chloride, corresponding to 500 ng/μL, 250 ng/μL, 100 ng/μL, 25 ng/μL, and 10 ng/μL of each phenol, were chromatographed using the revised recommended conditions.

The individual phenols in the test compound mixture were easily detected using FID at 10 ng injected on the column, except 4-nitrophenol and 4,6-dinitro-2-cresol, which were detected at a minimum of 25 ng injected.

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Two compounds, 4-methoxy phenol and 4-chloro-m-cresol, were not resolved using the GC conditions given. Attempts were made to resolve these two compounds by decreasing the column temperature program rate, but the two compounds were still not resolved. In GC/MS analysis, appropriate ions could be monitored by mass spectroscopy to distinguish the two compounds.

Standard solutions were prepared containing 1,2,4-trihydroxybenzene, 1,3-dihydroxybenzene, and 1,4-dihydroxybenzene, representative of MEG Category 18B - polyhydrics and dihydrics. Five hundred ng of each compound was injected on the column. These compounds were never detected and it is believed that they did not elute from the 1% SP 1240 DA GC column. The suggested alternative HPLC method would probably be more appropriate for these compounds.

Evidence concerning the precision and accuracy of this method of analyzing phenols is available from another program[10]. In that study, the following phenols were analyzed: 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, p-chloro-m-cresol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 4,6-dinitro-o-cresol, and 2,4-dimethyl phenol. A mixture of these phenols was added to raw municipal wastewater samples to give a concentration level of 50 μg/L. One liter aliquots of the water samples adjusted to a pH less than 2 were extracted three times with methylene chloride (250 mL, 100 mL, 100 mL). The concentrated extract was analyzed by GC/MS, using the 1% SP 1240 DA GC column. Replicate analyses relative to an internal standard were used to calculate precision and accuracy data.

The average recovery and range of relative standard deviations of each phenol follow:

Compound	Reporting Limit μg/L	Average Recovery	Range of Relative Standard Deviations
2-Chlorophenol	10	86	6-29
2-Nitrophenol	10-15	93	8-26
Phenol	10	60	20-26
2,4-Dimethylphenol	10	90	5-20
2,4-Dichlorophenol	10	103	9-15
2,4,6-Trichlorophenol	10	92	7-18
4-Chloro-3-cresol	10	98	12-17
2,4-Dinitrophenol	20-40	41	26-155
4,6-Dinitro-2-cresol	20-40	57	23-112
Pentachlorophenol	10-25	105	11-28
4-Nitrophenol	10-25	54	11-42

These data were accumulated over a period of two years.

In another study[49], microextraction was used to prepare aqueous samples for GC/FID analysis of phenols. In this study, a mixture of sixteen phenols were added to deionized, distilled, organic-free water. A 90 mL aliquot of the aqueous sample was adjusted to a pH < 2 and transferred to a volumetric flask containing 30 grams NaCl. One mL of diisopropyl ether was added to the sample. Extracts were analyzed by GC/FID, using a 1% SP 1240 DA GC column.

Average recoveries and ranges for duplicate samples follow:

Phenols*	Percent Recovery** (Range %)***
2-Chlorophenol	76(6.5)
2-Nitrophenol	68(9.4)
o-Bromophenol (IS)	81(4.9)
Phenol	54(1.1)
2-Bromo-4-methyl-phenol (IS)	84(2.8)
2,4-Dimethylphenol	83(0)
2,4-Dichlorophenol	89(2.5)
2,4,6-Trichlorophenol	89(3.2)
2,4-Dibromophenol (IS)	90(0)
4-Chloro-m-cresol	91(0)
2,3,4,6-Tetrachlorophenol (IS)	87(3.2)
2,4-Dinitrophenol	42(0)
4,6-Dinitro-o-cresol	77(3.6)
Pentachlorophenol	68(7.4)
p-Benzylphenol (IS)	87(0)
4-Nitrophenol	66(6.1)

*All phenols at a concentration level of 550 µg/L, except the dinitrophenols which were present at 1600 µg/L.

**Average Recovery based on duplicate samples.

***Range is the difference between duplicate recoveries expressed as a percent of the mean.

TABLE 34

Analytical Data for Phenols, Halophenols, and Nitrophenols

(MEG Categories 18, 19, 20)

MEG Category No.	Compound	Composition	MW	BP °C	GC Peak No.[a]	RRt[b]
19	2-Chlorophenol	C_6H_5OCl	128	175	1	.43
20	2-Nitrophenol	$C_6H_5NO_3$	139	216	2	.55
18-A	Phenol	C_6H_6O	94	182	3	.71
18-A	2-Ethylphenol	$C_8H_{10}O$	122	207	4	.83
18-A	2,4-Dimethylphenol	$C_8H_{10}O$	122	210	5	.85
19	2,4-Dichlorophenol	$C_6H_4OCl_2$	162	210	6	.88
18-A	3,4-Dimethylphenol	$C_8H_{10}O$	122	225	7	1.00
19	2,4,6-Trichlorophenol	$C_6H_3OCl_3$	197	246	8	1.07
18-A	4-Chloro-m-cresol	C_7H_7OCl	142	235	9	1.16
20	4-Methoxyphenol	$C_7H_8O_2$	124	243	9	1.16
19	2,4-Dinitrophenol	$C_6H_4N_2O_5$	184	Solid	10	1.19
20	4,6-Dinitro-o-cresol	$C_7H_6N_2O_5$	198	Solid	11	1.48
20	1-Naphthol	$C_{10}H_8O$	144	278	12	1.52
18-C	Pentachlorophenol	C_6HOCl_5	264	310	13	1.57
19	4-Nitrophenol	$C_6H_5NO_3$	139	279	14	2.18

(a) Numbers refer to gas chromatogram, Figure 32.

(b) Relative Retention Times (relative to 3,4-dimethylphenol, RT = 12 min.)

Sample: ~50 nanograms of each phenol in 1 μL CH_2Cl_2

Column: 1% SP 1240 DA, 100/120 mesh Supelcoport, 2m x 2mm glass

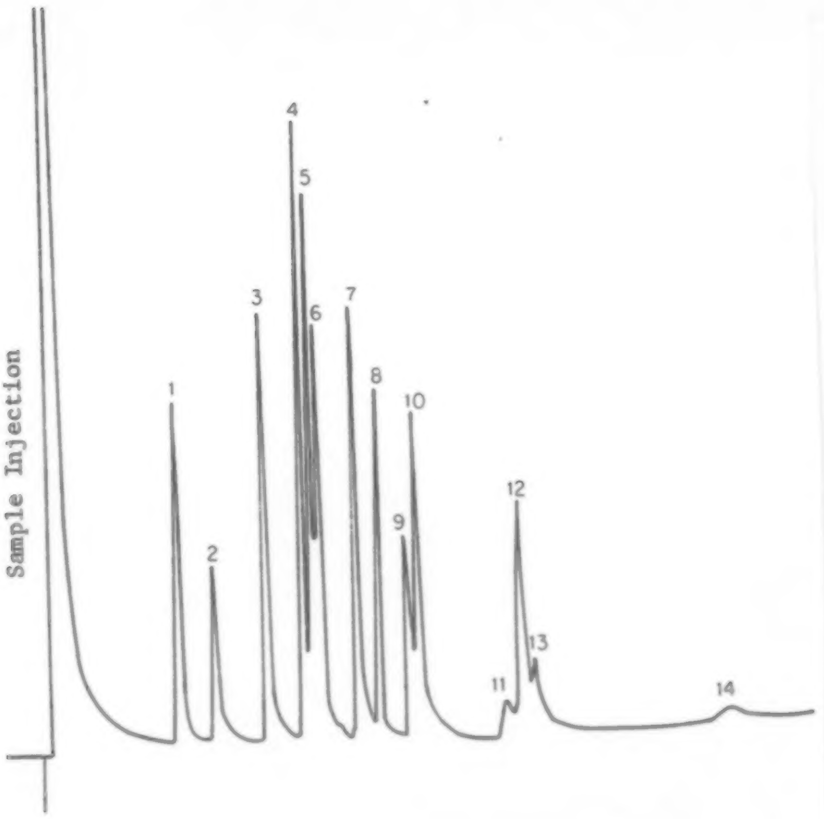
Column Temperature: 85°C (4 min.) $\xrightarrow{10°C/min.}$ 200°C (15 min.)

FID Detector Temperature: 275°C

Injector Temperature: 200°C

Attenuation Range: 8 x 10^{-11} amp/mV

Chart Speed: 0.5 cm/min.



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(GC peak numbers refer to Table 34)

Figure 32. Gas Chromatogram of Phenols, Halophenols, and Nitrophenols

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Polynuclear Aromatic Hydrocarbons (MEG Categories 21, 22)

The analytical method recommended for polynuclear aromatic compounds (MEG Categories 21, 22) is gas chromatography/mass spectroscopy. These categories include fused polycyclic hydrocarbons and fused non-alternate polycyclic hydrocarbons.

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POLYNUCLEAR AROMATIC HYDROCARBONS - (MEG CATEGORIES 21, 22)

Recommended Method

Recommended Method: GC/MS

Column: 3% Dexsil 400 on 100/120 mesh Chromosorb WAW, 3m x 2mm glass or stainless steel

Note: Silanized supports, e.g., Supelcoport, may be used when operating at temperatures less than 350°C. Silane groups bleed off at 350°C.

Example Conditions: Flow Rate: 30 mL/min.

Column Temperature: 100°C

$$\downarrow \; 8°C/min.$$

375°C

Lower Limit of Analysis: 10 ng injected (References 50,51,52)

Suggested Alternative Methods

1. GC/FID is an alternate detection system.
2. For very complex samples requiring greater separating power, capillary columns[48], for example, OV-17 glass capillary, .25mm x 25m. (Reference 48)
3. Reverse Phase HPLC/Fluorescence, UV Detection

Column: Perkin Elmer HC-ODS Sil-X reverse phase column, 2.6mm x 250mm

Detectors: UV, λ254 nm
Fluorescence, λ_{EX} 280 nm, λ_{EM} 389 nm

Example Conditions: Flow Rate: 0.5 mL/min.

Column Temperature: 40°C (CH_3CN in H_2O, isocratic 5 min.)

$$\downarrow$$

100°C (CH_3CN, isocratic 20 min.)

(Reference 53)

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Lower Limits of Analysis: 500 picograms injected, except napthalene and acenaphthylene - 10 nanograms injected and acenapthene, fluorene and phenanthrene - 5 nanograms injected.

The fluorescent selectivity and sensitivity for each polynuclear aromatic compound may be optimized by varying the excitation and emission wavelengths.

References

50. Lao, R.C., R.S. Thomas, H. Oja, L. Dubois, "Application of a GC/MS/Data Processing System Combination in the Analysis of the Polycyclic Aromatic Hydrocarbon Content of Airborn Pollutants," Analytical Chemistry, pp. 45, 908 (1973).

51. Cautreels, W., K. Van Cauivenberlke, "Fast Quantitative Analysis of Organic Compounds in Airborn Particulate Matter by Gas Chromatography with Selective MS Detection," J. Chromatography, pp. 151, 253 (1977).

52. Levins, P.L., C.E. Rechsteiner, Jr., and J.L. Stauffer, "Measurement of Polycyclic Organic Matter for Environmental Assessment," EPA-600/7-79-191, EPA/IERL, Contract No. 68-02-2150, August 1979.

53. Federal Register, December 3, 1979, Vol. 44, No. 233, pp. 69,514 - 69,517.

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POLYNUCLEAR AROMATIC HYDROCARBONS - (MEG CATEGORIES 21, 22)

Method Evaluation

One of the suggested alternative methods originally recommended for polynuclear aromatic hydrocarbons (MEG Categories 21 and 22) in the Level 2 Sampling and Analysis Manual was HPLC/Fluorescence. The suggested procedure has been used to analyze eighteen polynuclear aromatic hydrocarbons (PAH's) from napthalene to indeno(1,2,3-cd)pyrene with detection limits from 50 pg to 4 ng injected on the column.

The analytical finish for this category was evaluated using high performance liquid chromatography (HPLC) with fluorescent and ultraviolet (UV) detection. The details for the analytical method are given in the Recommended Procedure. A solvent program was used to elute the polynuclear aromatic compounds from a reverse phase HPLC column, HC-ODS Sil-X combining both isocratic and gradient elution techniques. The instrument system used consisted of Waters 6000A Pumps, a Waters 660 Solvent Programmer, a Waters 440A Absorbance Detector, and a Schoeffel FS 970 Fluorescence Detector. The HC-ODS Sil-X column was conditioned by running the solvent gradient elution program, recommended above, at least twice. The HPLC column was considered to be conditioned sufficiently when the fluorescent and UV base lines were smooth.

A test mixture was prepared in methylene chloride consisting of the compounds listed in Table 35. This test mixture was chromatographed on the HC-ODS Sil-X HPLC column, using the recommended conditions, to determine whether the individual compounds were adequately resolved. The UV detector, at a wavelength of 254 nm, was used to monitor napthalene and acenapthylene, while the remaining compounds were monitored by the fluorescence detector. A representative chromatogram is presented in Figure 33.

The retention times of each of the PAH compounds in the test mixture was determined by sequentially adding each of the polynuclear aromatic compounds to methylene chloride and chromatographing the solution after each addition, using the recommended method. Table 35 presents the relative retention times (RRT) of each of the PAH compounds in the test mixture. Two different compounds were used to calculate the RRT's, because two different detection systems were necessary to detect all the PAH compounds. Naphthalene and acenaphthylene were not detected by fluorescence. Naphthalene and acenaphthylene, detected by UV, are reported relative to acenaphthylene; while the other 13 PAH compounds, detected by fluorescence, are reported relative to benzo(a)anthracene.

The approximate detection limit for each polynuclear aromatic hydrocarbon (PAH) compound in the test mixture was determined. Two test mixtures, #1 and #2, were prepared in acetonitrile, corresponding to the concentration levels listed in Table 36.

Eight of the fifteen PAH's were detected with fluorescence at approximately 500 pg injected on column, using the λ_{EX} and λ_{EM} indicated.

Two of the eight detected PAH's, dibenz(a,h)anthracene and benz(g,h,i) perylene were not resolved at 500 pg injected, however, they were easily detected.

Acenaphthene, fluorene, and phenanthrene were not detected with fluorescence at approximately 500 pg injected. These three PAH's were detected at about 5 ng injected.

Napthalene and acenaphthylene were not detected by UV, $\lambda 254$, at 500 pg injected. However, these two compounds could be detected by UV at about 7 ng injected.

Fluorescent detection provides a convenient way of improving both the selectivity and sensitivity of HPLC analyses of PAH compounds. The fluorescent emission and excitation wavelengths may be varied to optimize both the detector sensitivity and selectivity for a particular PAH compound. Interfering PAH peaks may be removed from one another by varying the selectivity of detection. Further, optimization of the λ_{EX}, λ_{EM} for a particular PAH could increase the sensitivity by as much as a factor of 10, with subsequent lowering of the detection limit.

For example, the HPLC peaks attributable to benz(g,h,i)perylene and dibenz(a,h)anthracene were not well resolved using the recommended analytical conditions.

The fluorescent emission and excitation wavelengths may be varied to optimize the detector selectivity for one of the compounds of the pair. Benz(g,h,i)perylene has optimal sensitivity at λ_{EX} 302 nm and λ_{EM} 408 nm, while dibenz(a,h)anthracene has optional sensitivity at λ_{EX} 289 nm and λ_{EM} 378 nm.

This technique may be applied to many potentially unresolved pairs of polynuclear aromatic compounds. The λ_{EX} and λ_{EM} recommended in the alternative Level 2 Method were chosen to achieve good sensitivity and selectivity for all the polynuclear aromatic compounds, and therefore, were not necessarily optimal for any one particular PAH.

In another program[9], the procedure described in the Federal Register (Method 610-PAHs)[53], was evaluated. The Federal Register procedure includes sample preparation of aqueous samples by extraction into methylene chloride and silica gel chromatography and analysis using reverse phase HPLC with fluorescent detection.

As part of the evaluation of the Federal Register procedure[53], sixteen PAHs were added to clean water to give concentration levels between 0.8 µg/L and 50 µg/L. Some of the results are summarized in Table 37.

The HPLC analytical finish described in the Federal Register[53] is the same as that recommended as an alternative method (No. 3) for Level 2. The sample preparation steps described in the Federal Register[53] are applicable to aqueous samples being analyzed for PAHs during Level 2 studies.

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TABLE 35

Analytical Data for Polynuclear Aromatic Hydrocarbons

(MEG Categories 21, 22)

MEG Category No.	Compound	Composition	M.W.	HPLC[(a)] Peak No.	RRT[(b)]
21	Naphthalene	$C_{10}H_8$	128	1	.85
21	Acenapthylene	$C_{12}H_8$	152	2	1.0
21	Acenapthene	$C_{12}H_{10}$	154	3	.69
22	Fluorene	$C_{13}H_{10}$	166	4	.72
21	Phenanthrene	$C_{14}H_{10}$	178	5	.77
21	Anthracene	$C_{14}H_{10}$	178	6	.81
22	Fluoranthene	$C_{16}H_{10}$	202	7	.85
21	Pyrene	$C_{16}H_{10}$	202	8	.88
21	Benzo(a)Anthracene	$C_{18}H_{12}$	228	9	1.0
21	Chrysene	$C_{18}H_{12}$	228	10	1.03
22	Benzo[B]Fluoranthene	$C_{20}H_{12}$	252	11	1.11
22	Benzo[K]Fluoranthene	$C_{20}H_{12}$	252	12	1.16
21	Benzo(a) Pyrene	$C_{20}H_{12}$	256	13	1.18
21	Dibenz(a,h)Anthracene	$C_{22}H_{14}$	278	14	1.24
21	Benz(g,h,i)Perylene	$C_{22}H_{12}$	300	15	1.27

---

[a] Numbers refer to HPLC chromatogram, Figure 33.

[b] Relative Retention Times-Naphthalene and Acenaphthylene (Rt=15.9 min) were monitored by UV 254 nm; their retention times are relative to Acenapthylene. The remaining compounds were monitored by fluorescence and their retention times are relative to Benzo(a)Anthracene (Rt=32.5 min).

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Sample: Polynuclear Aromatic Compounds in 2 μL methylene chloride (nanograms injected, listed in Table 35)

Column: Perkin-Elmer, HC-ODS Sil-X reverse phase HPLC, 2.6mm x 250 mm O

Solvent Program: 40% CH_3CN in H_2O (isocratic, 5 min.)

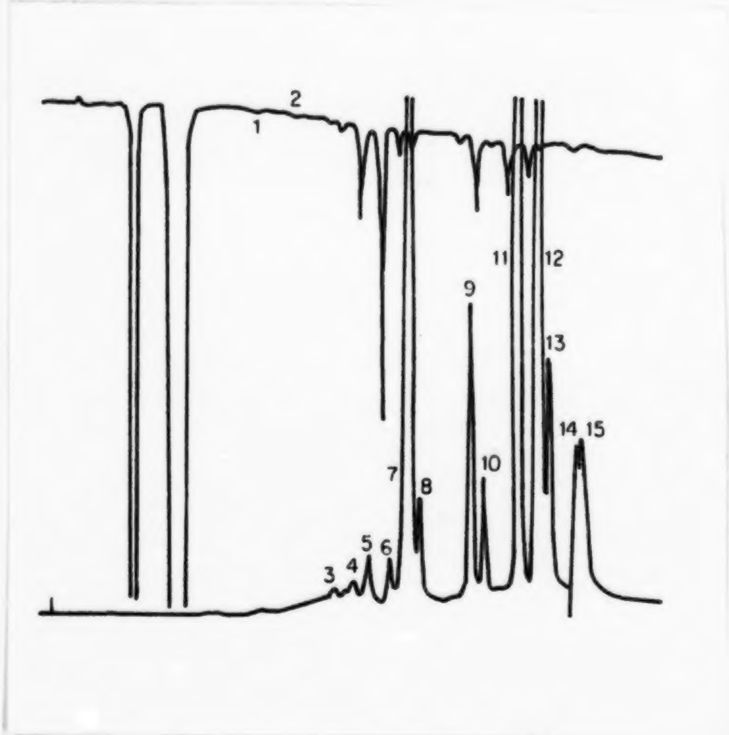
$\xrightarrow[\text{25 min.}]{\text{Linear Gradient}}$ 100% CH_3CN (isocratic, 20 min.)

Flow Rate: 0.5 mL/min.

Detectors: UV (λ:254 nm), Range = x.05 absorbance units full scale

Fluorescence:
EX = 280 nm
EM 389 nm filter
Range = x 1.0 microamps
Time Constant = 7 seconds

Chart Speed: 0.2 in/min.



(GC peak numbers refer to Table 35)

Figure 33. Gas Chromatogram of Polynuclear Aromatic Hydrocarbons (Test Mixture 1)

TABLE 36

Concentration Data for Test Mixtures of Polynuclear Aromatic Hydrocarbons

(MEG Categories 21, 22)

Pk #	PAH	Test Mixture #1 ng inj	Test Mixture #2 ng inj
1	Naphthalene	5.0	0.637[1]
2	Acenaphthylene	7.6	0.511[1]
3	Acenapthene	9.6	0.511[2]
4	Fluorene	3.4	0.500[2]
5	Phananthrene	5.0	0.614[2]
6	Anthracene	3.4	0.535
7	Fluoranthene	8.8	0.504
8	Pyrene	6.8	0.510
9	Benzo(a)anthracene	5.4	0.506
10	Chrysene	3.4	0.507
11	Benzo[b]fluoranthene	3.4	0.500
12	Benzo[k]fluoranthene	3.4	0.500
13	Benzo(a)pyrene	5.2	0.545
14	Dibenz(a,h)anthracene	5.2	0.565
15	Benz(g,h,i)perylene	3.8	0.500

---

[1] Not detected by UV, $\lambda 254$.

[2] Not detected at these concentrations by fluorescence $\lambda_{EX} = 280$ and $\lambda_{EM} \geq 389$.

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TABLE 37

Quality Control Data for Polynuclear Aromatic Hydrocarbons Using Federal Register Method 610[49]

(MEG Categories 21, 22)

Compound	Average Recovery*		Standard Deviation
Naphthalene	75.9	±	9.3
Acenaphthylene	77.4	±	7.1
Acenaphthene	79.8	±	6.9
Fluorene	46.4	±	12.8
Phenanthrene	90.5	±	8.2
Anthracene	89	±	6
Fluoranthene	88.7	±	4.8
Pyrene	92.4	±	2.0
Benzo(a)anthracene	99.1	±	1.9
Chrysene	102	±	13.9
Benzo(b)fluoranthene	87.6	±	5.1
Benzo(k)fluoranthene	86.1	±	6.9
Benzo(a)pyrene	90.6	±	6.9
Dibenzo(a,h)anthracene	87	±	4.5
Benzo(g,h,i)perylene	87	±	4.5
Indeno(1,2,3-cd)pyrene	84.2	±	5.5

* Based on 4 data points.

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Heterocyclic Nitrogen Compounds (MEG Category 23)

The analytical method for heterocyclic nitrogen compounds (MEG Category 23) is gas chromatography/mass spectroscopy.

The compounds included in this category are divided into four subcategories:

Pyridine and Substituted Pyridines (23A)
Fused 6-Membered Ring Heterocycles (23B)
Pyrrole and Fused Ring Derivatives of Pyrrole (23C)
Nitrogen Heterocycles Containing Additional Heteroatoms (23D)

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HETEROCYCLIC NITROGEN COMPOUNDS - (MEG CATEGORY 23)

Recommended Method

Recommended Method: GC/MS

Column: 3% Dexsil 400 on 100/120 mesh Supelcoport, 3m x 2mm glass or stainless steel (Reference 52)

Example Conditions: Carrier Gas: 30 mL/min., Helium

Column Temperature: 75°C (isothermal, 2 minutes)
↓ 8°C/min.
323°C

Injector: 225°C

Lower Limit of Analysis: 10 ng injected, except pyrrole and pyridine - 50 ng injected

Suggested Alternative Methods

1. GC/AFID or GC/FID for samples free of interferences or preliminary evaluation.

   Flame Ionization Detector: 275°C

   GC/FID Lower Limit of Analysis: 10 ng injected, except pyrrole and pyridine - 100 ng injected

2. For complex samples requiring greater separating power:

   Column: SE-52 glass capillary - average thickness: 29μ

   Example Condiiions: Column Temperature: 100°C
   ↓ 4°C/min.
   280°C (Reference 52)

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References

52. Levins, P.L., C.E. Rechsteiner, Jr., and J.L. Stauffer, "Measurement of Polycyclic Organic Matter for Environmental Assessment," EPA-600/7-79-191, EPA/IERL, Contract No. 68-02-2150, August 1979.

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HETEROCYCLIC NITROGEN COMPOUNDS - (MEG Category 23)

Method Evaluation

The analytical method originally recommended for heterocyclic nitrogen compounds (MEG Category 23) in the Level 2 Sampling and Analysis Manual was:

Column: 3% Dexsil 400 on 100/120 mesh Supelcoport,
3m x 2mm glass or stainless steel

Example Conditions: Flow Rate: 60 mL/min

Column
Temperature: 160°C
↓ 8°C/min.
300°C

The analytical finish for this category was evaluated using gas chromatography/flame ionization detection, GC/FID, to verify the appropriateness of the GC conditions. The instrument used was a Varian 2700 Gas Chromatograph. The GC column, 3% Dexsil 400 on 100/120 mesh Supelcoport was conditioned overnight at 350°C.

A test mixture was prepared consisting of the compounds listed in Table 38 in methylene chloride. This test mixture was chromatographed at the recommended conditions on the 3% Dexsil 400 GC column to determine whether the individual compounds were adequately resolved.

The original method recommended that the column be temperature programmed from 160°C to 300°C at 8°C per minute; this was changed to programming from 75°C (2 min., isothermal) to 300°C at 10°C per minute. This change was made to resolve the GC peaks of the low boiling heterocyclic nitrogen compounds, e.g., pyrrole, b.p. 130°C and pyridine, b.p. 116°C, from the methylene chloride GC solvent peak.

It was necessary to determine the GC peak retention times of each heterocyclic nitrogen compound in the test mixture. The retention times were determined by sequentially adding each of the heterocyclic nitrogen compounds to methylene chloride and chromatographing the solution after each addition, using the revised recommended conditions.

The two compounds, pyrrole and pyridine, were not well resolved from the methylene chloride solvent GC peak. In GC/MS analysis, appropriate ions could be monitored by mass spectroscopy to distinguish the two compounds.

The detection limit for each heterocyclic nitrogen compound was determined. One test mixture contained the heterocyclic nitrogen compounds at a level of 100 ng/μL of each compound except for pyridine, which was at a concentration of 1.00 μg/μL. A second mixture at 10 times lower concentration was prepared. The individual heterocyclic nitrogen compounds were easily detected using FID at 10 ng, except for pyridine which had a minimum detection limit of 100 ng and pyrrole which was unresolved from the solvent GC peak at levels less than 100 ng.

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TABLE 38

Analytical Data for Heterocyclic Nitrogen Compounds

MEG Category 23)

MEG Category No.	Compound	Composition	MW	BP(°C)	GC Peak No. (a)	RRT (b)
23C	Pyrrole	C_4H_5N	67	130	1	.12
23A	Pyridine	C_5H_5N	79	116	2	.15
23D	Benzothiazole	$C_7H_5N_5$	135	231	3	.84
23C	3-Methyl indole	C_9H_9N	131	266	4	1.00
23B	Acridine	$C_{13}H_9N$	179	345	5	1.45
23C	Carbazole	$C_{12}H_9N$	167	355	6	1.48

(a) Numbers refer to gas chromatograph, Figure 34.

(b) Relative Retention Times (relative to 3-methyl indole, RT = 14.6 min.)

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Sample: ∿100 nanograms each heterocyclic nitrogen compound, except pyridine 1.0 μg in 1.0 μL methylene chloride

Column: 3% Dexsil 400, 100/120 mesh Supelcoport, 3m x 2mm glass

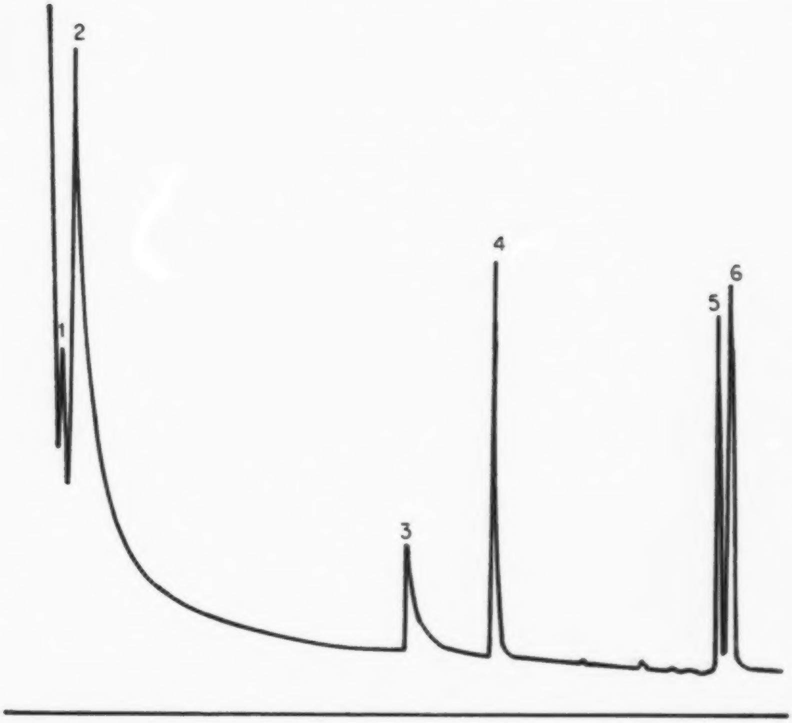
Column Temperature: 75°C (2 min) $\xrightarrow{10^\circ\text{C/min}}$ 300°C

Injector Temperature: 225°C

FI Detector Temperature: 275°C

Attenuation x Range: 4×10^{-11} amp/mV

Chart Speed: 0.5 cm/min.



(GC peak numbers refer to Table 38)

Figure 34. Gas Chromatogram of Heterocyclic Nitrogen Compounds

Heterocyclic Oxygen Compounds (MEG Category 24)

The analytical method for heterocyclic oxygen compounds (MEG Category 24) is gas chromatography/mass spectroscopy. This procedure was not evaluated for this program.

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HETEROCYCLIC OXYGEN COMPOUNDS - (DMEG CATEGORY 24)

Recommended Method

Recommended Method: GC/MS

Column: 3% SP 1000 on 100/120 mesh Supelcoport, 2m x 2mm glass column

Example Conditions: Flow Rate: 30 mL/min.

Column Temperature: 100°C
↓ 10°C/min.
250°C

Detection Limit: 10 ng injected

Suggested Alternative Methods

1. GC/FID for preliminary evaluation or samples free of interferences.
2. Additional resolutions may be obtained using the alternate column described for MEG Category 23, Capillary OV-17.

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Heterocyclic Sulfur Compounds (MEG Category 25)

The analytical method recommended for heterocyclic sulfur compounds (MEG category 25) is gas chromatography/mass spectroscopy. Gas chromatography columns are recommended for species within particular boiling point ranges. These boiling point ranges overlap, thus offering flexibility when choosing a gas chromatography column for a Level 2 analysis.

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HETEROCYCLIC SULFUR COMPOUNDS - (MEG CATEGORY 25)

Recommended Method

Recommended Method: GC/MS

A. Species with Boiling Points in the Range 80°C to 200°C

Column: 0.1% SP 1000 on Carbopack C 80/100 mesh, 2m x 2mm glass column

(Injection volumes ≤ 0.5 μL are recommended)

Example Conditions: Carrier Gas: 30 mL/min., Helium

Column Temperature: 70°C
↓ 10°C/min.
220°C

Injector Temperature: 230°C

Lower Limit of Analysis: 3 ng injected

B. Species with Boiling Points Greater than 110°C

Column: 3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm glass

Examples Conditions: Carrier Gas: 20 mL/min., Helium

Column Temperature: 70°C (2 min.)
↓ 10°C/min
350°C

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Injector Temperature: 285°C

Lower Limit of Analysis: 5 ng injected

Suggested Alternative Methods

1. GC/Flame Photometric Detection or GC/FID for preliminary evaluation or for samples free of inteferences.
    a. For species with boiling point range 80°C to 200°C.

    Flame Ionization Detector Temperature: 250°C

    Flame Ionization Lower Limit of Analysis: 5 ng injected

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b. For species with boiling point >110°C.

Flame Ionization Detector Temperature: 325°C

Flame Ionization Lower Limit of Analysis: 5 ng injected

HETEROCYCLIC SULFUR COMPOUNDS (MEG CATEGORY 25)

Method Evaluation

A. Species with Boiling Point 80°C to 200°C

The analytical method originally recommended for heterocyclic sulfur compounds with boiling points from 80°C to 200°C in the Level 2 Sampling nad Analysis Manual was:

Column: 0.1% SP 1000 on Carbopack C, 80/100 mesh Supelcoport, 2m x 2mm glass or stainless steel

Example Conditions: Flow Rate: 30 mL/min.

Column Temperature: Isothermal at 225°C

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Hewlett Packard 5840A Gas Chromatograph. The recommended GC column, 0.1% SP 1000 on 80/100 mesh Carbopack C, was conditioned overnight at 180°C and then three hours at 225°C.

A test mixture was prepared consisting of the heterocyclic sulfur compounds listed in Table 39 in methylene chloride. This test mixture was chromatographed on the 0.1% SP 1000 column, using the recommended conditions, to determine whether the individual compounds were adequately resolved. It was necessary to use sample injection volumes ≤ 0.5 μL to avoid plugging of the 0.1% SP 1000 Carbopack C GC column. The original method recommended a column temperature of 225°C isothermal; this was changed to column temperature programming from 70°C to 2,200°C (isothermal, 20 minutes) at 10°C per minute. This change to a lower initial temperature was made to resolve the low boiling heterocyclic sulfur compounds from the solvent GC peak.

It was necessary to determine the GC peak retention time for each heterocyclic sulfur compound in the test mixture. The retention times were determined by sequentially adding each of the heterocyclic sulfur compounds to the methylene chloride and chromatographing the solution after each addition. The retention times for each compound in the test mixture are listed in Table 39. A representative gas chromatogram is presented in Figure 35.

The detection limit for each heterocyclic sulfur compound was determined. A test mixture was prepared in methylene chloride to give a concentration level of 6 ng/μL of each heterocyclic sulfur compound listed in

Table 39. The individual heterocyclic sulfur compounds were detected at 3 ng injected on column, using the revised recommended conditions.

Note that it is not advisable to try to push this method for analysis of heterocyclic sulfur compounds with boiling points above 200°C. That would require prolonged use of the column at temperatures near its upper limit of 225°C, with consequent dramatic reduction in column life. An alternative method for higher boiling heterocyclic sulfur compounds is given in the next section.

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TABLE 39

Analytical Data for Heterocyclic Sulfur Compounds with Boiling Points 80°C to 200°C

(MEG Category 25)

MEG Category No.	Compound	Compostition	MW	BP, °C	GC[(a)] Peak No.	RRT[(b)]
25	Thiophene	C_4H_4S	84	84	1	0.30
25	2-Methylthiophene	C_5H_6S	98	113	2	0.63
25	2,5-Dimethylthiophene	C_6H_8S	112	134	3	1.00
25	Benzo(b)thiophene	C_8H_6S	134	221	4	1.98

(a) Numbers refer to gas chromatogram, Figure 35.

(b) Relative Retention Times (relative to 2,5-dimethylthiophene, RT = 13.76 min.)

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Sample: 60 nanograms of each heterocyclic sulfur compound in 0.5 μL methylene chloride

Column: 0.1% SP 1000 on 80/100 mesh Carbopak C, 2mm x 2mm glass

Flow Rate: 30 mL/min., Helium

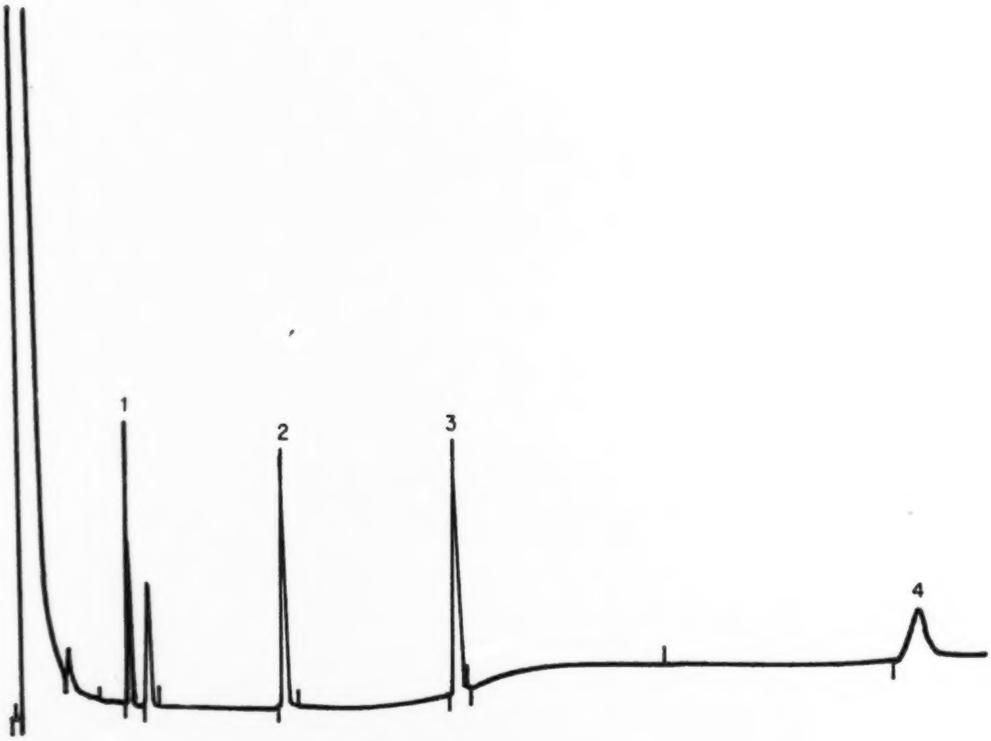
Column Temperature: 70°C $\xrightarrow{10^\circ\text{C/min.}}$ 200°C (20 min.)

Injector Temperature: 230°C

FID Detector Temperature: 250°C

Attenuation: 2^8

Chart Speed: 0.5 cm/min.



(GC peak numbers refer to Table 39)

Figure 35. Gas Chromatogram of Heterocyclic Sulfur Compounds with Boiling Points 80°C to 200°C

B. Species with Boiling Points greater than 110°C

The analytical method which has been recommended for heterocyclic sulfur compounds with boiling points greater than 110°C in the Level 2 Sampling and Analysis Manual was:

Column:	3% SP 2250 on 100/120 mesh Supelcoport, 2m x 2mm glass or stainless steel	
Example Conditions:	Column Temperature:	70°C ↓ 10°C/min. 350°C
Detection Limit:	10 ng injected	

The recommended analytical finish for this category was evaluated using gas chromatography/flame ionization detection (GC/FID). The instrument used was a Hewlett Packard 5840A Gas Chromatograph. The recommended column, 3% SP 2250 on 100/120 mesh Supelcoport was conditioned overnight at 340°C.

A test mixture was prepared consisting of the heterocyclic sulfur compounds listed in Table 40 in methylene chloride. This test mixture was chromatographed on the 3% SP 2250 GC column using the recommended conditions. The original method recommended the column be temperature programmed from 70°C to 350°C at 10°C per minute; this was changed to a reduced upper temperature (260°C), since 260°C was sufficient to elute all the compounds in the test mixture. This upper temperature may have to be increased when analyzing an enviornmental sample in which higher boiling heterocyclic sulfur compounds may be present.

It was necessary to determine the GC peak retention time for each heterocyclic sulfur compound in the test mixture. The retention times were determined by sequentially adding each of the compounds to methylene chloride and chromatographing the solution after each addition, using the revised recommended conditions. Retention times for each of the heterocyclic sulfur compounds in the test mixture are presented in Table 40. A representative gas chromatogram is presented in Figure 36.

The detection limit for each heterocyclic sulfur compound was determined. A mixture of the compounds was prepared at a concentration of 5 ng/μL. This mixture was chromatographed using the revised recommended conditions. Each compound was detected, although 2-methylthiophene was not well resolved from the methylene chloride solvent peak. Slight modifications of the GC column temperature program would improve the resolution of the GC peaks attributable to the low boiling heterocyclic sulfur compounds from the methylene chloride solvent GC peak.

TABLE 40

Analytical Data for Heterocyclic Sulfur Compounds with Boiling Points greater than 110°C

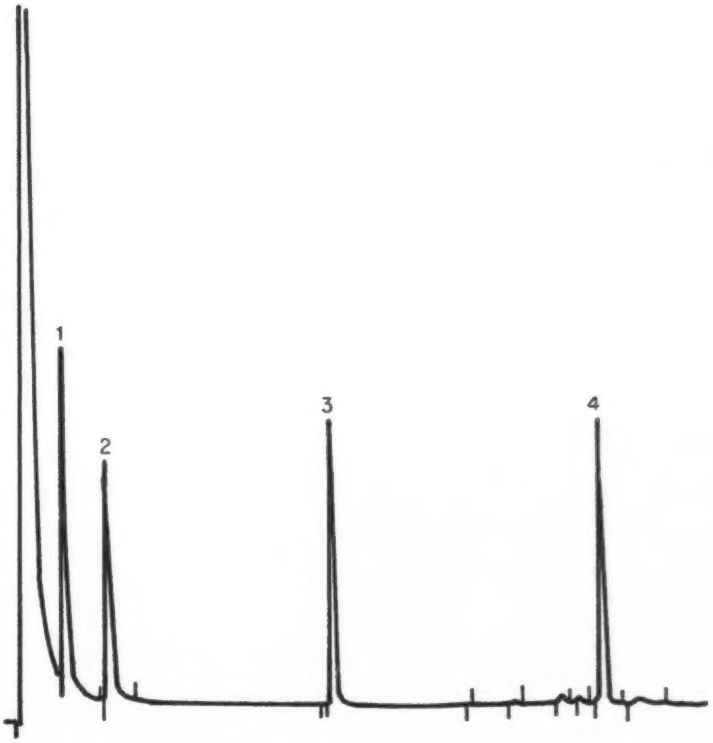
(MEG Category 25)

MEG Category No.	Compound	Composition	MW	BP, °C	GC[a] Peak No.	RRT[b]
25	2-Methylthiophene	C_5H_6S	98	113	1	0.20
25	2,5-Dimethylthiophene	C_6H_8S	112	134	2	0.31
25	Benzo(b)thiophene	C_8H_6S	134	221	3	1.00
25	Dibenzothiophene	$C_{12}H_8S$	184	332	4	2.00

(a) Numbers refer to gas chromatogram, Figure 36.

(b) Relative Retention Times (relative to benzo(b)thiophene, RT = 9.6 min.)

Sample:	125 nanograms of each heterocyclic sulfur compound in 1 μL methylene chloride
Column:	3% SP 2250 on 100/120 mesh Supelcoport, 2mm x 2mm glass
Flow Rate:	20 mL/min., Helium
Column Temperature:	70°C (2 min.) $\xrightarrow{10^{\circ}\text{C/min.}}$ 260°C
Injector Temperature:	285°C
FI Detector Temperature:	325°C
Attenuation:	2 ↑ 8
Chart Speed:	0.5 cm/min.



(GC peak numbers refer to Table 40)

Figure 36. Gas Chromatogram of Heterocyclic Sulfur Compounds with Boiling Points greater than 110°C

Recovery Studies

The precision and accuracy of the Heterocyclic Sulfur Compound methods were investigated. A mixture of the heterocyclic sulfur compounds listed in Table 41 was added into clean water to give a concentration level of 500 μg/L. One liter aliquots of the water samples and blank samples were extracted three times with methylene chloride (250 mL:100 mL:100 mL). These extracts were dried by passing them through sodium sulfate and were concentrated to 10 mLs using a Kuderna Danish (KD) Evaporator. These concentrated extracts were then analyzed by GC/FID, on 0.1% SP 1000, 80/100 Carbopack C (b.p. range 80°C-200°C) and 3% SP 2250, 100/120 Supelcoport (b.p. range >110°C), using the recommended conditions. The recoveries $(\overline{P})$ and standard deviation (Sp) of replicate analyses at the extraction and concentration step are listed in Table 41.

The extracts were then chromatographed on silica gel, using the procedure described in the IERL/RTP Procedures Manual; Level 1 Environmental Assessment (Second Edition), October 1978. The seven silica gel fractions were analyzed using GC/FID, as previously described. The first three fractions contained all the heterocyclic sulfur compounds, however, the concentration levels were too low to accurately quantify, therefore, the first three fractions were combined and concentrated using a KD evaporator. The recovery data for the extraction/silica gel procedure are presented in Table 41. It was not possible to detect for thiophene due to interferences from the solvent.

The silica gel chromatography alone was studied to determine the recovery of each heterocyclic sulfur compound and the fraction in which each heterocyclic sulfur compound eluted. Two replicate mixtures of the heterocyclic sulfur compounds listed in Table 41 were prepared in cyclopentane to give a concentration level of 250 μg/mL. Pentadecane and Naphthalene were also added to the two test mixtures to verify the silica gel elution pattern. The two test mixtures and a reagent blank were chromatographed on and eluted from the silica gel, using the Level 1 procedures. The silica gel fractions were analyzed by GC/FID, as described previously. The recoveries (P), average recoveries $(\overline{P})$, and the fraction number in which each heterocyclic sulfur compound eluted are listed in Table 41. Thiophene was not analyzed due to the interferences from the cyclopentane solvent. Pentadecane eluted in fraction 1 and naphthalene eluted in fraction 2, which confirms that the silica gel column was giving an appropriate elution pattern.

The recoveries listed for the silica gel procedure alone agree well with the recoveries listed for the combined extraction/silica gel procedure listed in Table 41. Theoretical recoveries for the combined extraction/silica gel procedure were calculated as the product of the average recoveries of extraction procedure alone and the silica gel procedure alone. The theoretical and measured recoveries for the combined extraction/silica gel procedure are listed below:

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Compound	Calculated Combined Recovery	Measured Combined Recovery
2-Methylthiophene	32	33
2,5-Dimethylthiophene	31	35
Benzo(b)thiophene	62	54
Dibenzothiophene	57	64

The measured recovery and precision are very close to those calculated for the combined extraction/silica gel procedure. One can, therefore, be confident that a correction factor may be used to claculate the concentration level of a particular heterocyclic sulfur compound in an aqueous sample.

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TABLE 41

Recovery Data for Heterocyclic Sulfur Compounds

(MEG Category 25)

			Extraction			Extraction Silica Gel			Silica Gel		
Compound	BP, °C	Quantification Method(a)	P	$\overline{P}$	Sp	P	$\overline{P}$	Sp	P	$\overline{P}$	Silica Gel Fraction #
Thiophene	84	1	43 75 69	62	17.0	Could not be Detected(b) Detected			Could not be Detected (b) Detected		
2-Methylthiophene	113	1	74 68 83	75	8	41 17 42	33	14.2	37 48	42	1
2,5-Dimethylthiophene	134	2	88 53 79	73	18.2	38 21 46	35	12.8	37 48	42	1,2
Benzo(b)thiophene	221	2	86 80 80	82	4	53 44 65	54	105	77 73	75	2
Dibenzo(b)thiophene	332	2	81 83 77	80	3	58 61 72	64	7	72 70	71	2,3

(a) Method 1 - Revised Recommendation for Heterocyclic Sulfur Compounds with boiling points from 80°C to 200°C

Method 2 - Revised Recommendation for Heterocyclic Sulfur Compounds with boiling points greater that 110°C

(b) Thiophene was not analyzed due to pentane solvent GC peak interferences

V. APPLICATION TO A REAL SAMPLE

In the previous sections of this report, the philosophy as well as the analytical methodology involved in undertaking a Level 2 study were discussed. In this section, a partial Level 2 analysis of a combustion effluent from a coal preheater facility is described to illustrate the ideas and methods presented previously. The ideas and methods discussed include:

- iterative examination ("looping") of the Level 1 data to determine if the flagged categories in a sample do, in fact, require Level 2 analysis
- analytical finish selection pertinent to the category(s) of interest
- analytical methods selection pertinent to the goals of the overall sampling and analysis program (i.e., calibration methods, standards, quality control and quality assurance procedures).

A. Introduction

The expected goal of a Level 2 analysis is a more complete characterization of the sample in terms of those compound classes which were flagged by Level 1 as being of environmental concern in order to define the specific components of the effluent stream which need to be controlled, e.g., in Level 3. If a Level 1 organic analysis of a sample identifies one or more chemical classes as present in quantities exceeding the level of concern, such as the worst case MEG[2] values for the specific compound class, a more extensive examination of the Level 1 data is undertaken as the first step prior to any Level 2 sampling and analyses. The more complete examination of the Level 2 data allows determination of the appropriateness of the worst case decision criteria and may, in fact, show that the Level 1 report sufficiently characterizes the sample for some of the compound categories to obviate the need for further Level 2 work directed towards those categories. This procedure is analogous to "looping", which is described in additional detail in an Appendix to the full report.

A simple example of the "looping" approach for examining Level 1 data is as follows. A hypothetical air sample, analyzed by Level 1 methods, could be shown to contain fused polycyclic aromatic hydrocarbons (MEG Category 21) at a level of 1.3×10^3 μg/m^3. This total level of MEG Category 21 compounds in the sample exceeds the worst case DMEG level for that category, which is 2×10^{-2} μg/m^3 for benzo(a)pyrene. A Level 2 study might, therefore, seem to be required. Application of the looping approach, however, could show that no benzo(a)pyrene is present and that the worst case DMEG value is, therefore, not appropriate. Looping would involve reexamination of the Level 1 LRMS reports which might show, for example, that the only polycyclic aromatic hydrocarbons detected in the

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sample were naphthalene (DMEG = 5 x 10^4 μg/m^3), phenanthrene (DMEG = 1.6 x 10^3 μg/m^3) and pyrene (DMEG = 2.3 x 10^5 μg/m^3). The total level of MEG Category 21 compounds in the sample is lower than any of these DMEG values. Thus, although the worst case decision criterion would have indicated a need for further analysis of this sample, looping showed that Level 2 analysis is not needed.

The hypothetical example can be extended to illustrate that the looping approach results in selection of a DMEG decision criterion which is the probable worst case value for that range of compounds within a category that are or may be present (i.e., cannot be ruled out) in the sample. If the Level 1 analysis showed a total level of 3 x 10^5 μg/m^3 for MEG Category 21 and the LRMS report again indicated that naphthalene, phenanthrene and pyrene were the species responsible for the category assignment, then the appropriate worst case DMEG for this sample would be that for phenthrene (2 x 10^3 μg/m^3). Since the total level exceeds this DMEG value, the category must be dealt with further. For this particularly simple example, however, it would probably not be necessary to conduct a separate analysis to generate compound specific data. The Level 1 LRMS relative abundance data could be reexamined to provide estimates of the abundance of each of the three specific compounds present in the sample , and this might suffice for Level 2 purposes. A Level 2 analysis by GC/MS or HPLC would be warranted only if there were an explicit need for better quantitative data in a particular study.

Following the detailed examination of the Level 1 data, Level 2 sampling and analysis efforts would begin for those MEG categories flagged during the Level 1 analysis as being of environmental concern. The sampling effort for a Level 2 study may involve collection of additional samples - gas, liquid, solid, etc. - from the source under study or depending upon the goals of the overall program, the previously collected Level 1 samples may be used for the Level 2 effort provided the Level 1 samples have been appropriately stored. Analytical methods, such as those described in Chapter IV would be applied to the sample for each of the MEG categories of concern.

This scenario points out several important features of the Level 2 analysis. Such an analysis is directed by the findings of some previous body of work, which will usually be the Level 1 survey of the sample. The analytical procedures used for Level 2 need to be specific for each class of compound (or functionality) under examination and yield accurate quantitative data. Hence, the set of analytical procedures used for the Level 2 analysis of a particular sample should provide confirmation of the identification made during the Level 1 analysis, as well as the quantitative information pertinent to each identified compound.

This chapter describes the results of a partial analysis of a real sample of the organics collected by a SASS train using Level 2 methods. The Level 2 analysis involves several approaches of which three will be illustrated in the following discussion. Each chemical class of interest could be analyzed using the optimized conditions for that category, described in

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Section IV (Method A). Following tentative identification of all of the constituents in the sample for that class, the identity of each constituent would be confirmed and quantified through the analysis of spiked samples and calibration curves. With such an approach, the quantitative accuracy of the Level 2 report could be improved using specific compound recovery data obtained during the spiked sample experiments. Such an approach would typically require multiple analyses, each restricted to one of the chemical classes of interest.

Alternatively (Method B), the Level 2 analysis approach might be focused on the particular compounds which are considered to be the most hazardous for each of the categories identified by Level 1. Such an approach might involve the use of an external calibration curve, literature retention data for the specific compounds under the chosen chromatographic system, and spectral matching to identify and quantify the components in the sample. In either of these first two alternative approaches, the sample is examined serially for the chemical class(es) of interest as determined during the Level 1 study.

A third approach (Method C) would be to analyze the sample via the recommended Level 2 procedures for the chemical class(es) of major interest, but, to examine the output of each analysis for information concerning all identifiable components in addition to those for which the specific Level 2 analysis procedure was targetted. Many of the analytical methods listed in Section IV share common features, i.e., they use the same chromatography columns and use essentially the same chromatography conditions, which allows several chemical classes to be examined at the same time. This approach is designed to maximize the information obtained concerning the sample while minimizing analysis time and expense. This approach may also incorporate provisions for confirmation of compound identity and for determination of recovery by spiking of samples or by reference to the literature. Examples which correspond to each of these types of approaches will be discussed in this chapter by application to a partial Level 2 analysis of a SASS train sample.

Part of the planning in the approach to a Level 2 analysis involves consideration of the characteristics of the detection system. As mentioned previously, the detector utilized in the analytical finish of a Level 2 study should allow specific detection of compounds within the class of interest. The detector may react selectively to the chemical functionality defining the compound category of interest, such as an ECD for halogen-containing compounds, or a GC/FTIR combination for ketones, esters, etc.; alternatively, a mass spectrometric detection system, which allows identification of individual constituents per se, may be used. In this case, the analyst sorts the compound identifications into the proper categories. In a Level 2 study where only one compound class (or functionality) is of concern and any other categories found by Level 1 will not pose interference problems, the selective detectors, such as ECD or FTIR would be appropriate and cost effective. On the other hand, a Level 2 study in which one attempts to characterize a wider range of the sample components would probably be best suited to using MS detection.

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For the sample considered in this chapter, all of the analyses use MS detection as the analytical finish.

B. Sample and Method Selection

A sample of the effluent from a coal preheater facility was chosen for examination to illustrate a partial Level 2 analysis. This sample represents the pooled extracts of a SASS train stack sample obtained upstream of the air pollution control device (a wet scrubber). Reasons for selection of this sample for Level 2 analysis were:

1. It represents a complex environmental sample;
2. The emissions of the facilities are similar to those expected from other conventional combustion processes;
3. Complete Level 1 data were available for this sample;
4. Several categories of compounds were present at levels high enough to warrant Level 2 analysis by DMEG criteria.

Table 42 summarizes the Level 1 results. Tables 43 through 50 provide supporting information; the Level 1 organic summary table, including quantitative TCO and GRAV data for each LC fraction; and the corresponding Level 1 LRMS reports. The data in these tables are used for the initial examination of the sample (looping) to determine which compound classes require Level 2 efforts.

The results of the Level 1 analysis show that five of the six MEG categories identified in the sample are present at levels which exceed the worst case DMEG value for those categories. Prior to initiating a Level 2 effort for all of those categories of compounds, the Level 1 data for this sample needs to be examined to determine the appropriateness of the worst case DMEG criteria.

Esters, MEG Category 8d, are present at a level two orders of magnitude higher than the worst case DMEG level for this compound class. Examination of the Level 1 data for those LC fractions containing esters, shown in Tables 47 through 50, shows that phthalates are the only esters present with dioctyl and dibutyl phthalate accounting for more than 95% of this category. The DMEG value for either of these phthalates is 5 mg/m^3, which is lower than their level in the sample. Hence, analysis by Level 2 methods is indicated. The separate question of the appropriateness of undertaking a Level 2 study and its associated expense for this category of compounds, which has been fairly well characterized by Level 1, is dependent upon the program goals for which the Level 1 effort was undertaken. For the purposes of illustration in this report, we have assumed that the Level 1 data characterizes this compound class sufficiently to meet the goals of the program. Hence, no specific Level 2 effort will be directed towards the esters category.

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TABLE 42

Summary of Level 1 Organic Analysis Results

MEG No.	Category	Concentration in Effluent (mg/m^3)	Worst Case DMEG (mg/m^3)
1	Aliphatic Hydrocarbons, >100°C boiling point	190	1500
21,22	Fused Aromatic Hydrocarbons, m/z <216	340	1.6
21,22	Fused Aromatic Hydrocarbons, m/z >216	280	2×10^{-5}
23	Heterocyclic N Compounds	20	.01
8	Esters	150	1.0
18	Phenols	120	2.0
	Unclassified	20	-

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TABLE 43

ORGANIC EXTRACT SUMMARY TABLE

Sample 2A Inlet, Stack Sample

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m³	188	520	87	23	33	213	40	1100
TCO, mg	111	305	34	7.7	12	43	13	530
GRAV, mg	130	360	78	22	30	230	38	890

Category Int/mg/m³

Aliphatic Hydrocarbons	10/188							190
Fused Aromatics, <216 m/e*		100/260	100/73	100/5.6	10/2.4			340
Fused Aromatics, >216 m/e*		100/260	10/7.3	100/5.6	10/2.4			280
Heterocyclic N Compounds				100/5.6	10/2.4	10/9.7	10/1.9	20
Esters				100/5.6	100/24	100/97	100/19	150
Phenols						100/97	100/19	120
Unclassified			10/7.3	10/0.6	10/2.4	10/9.7	1/0.2	20

*For the purposes of this report, the biphenyls were accounted for in the Fused Aromatics categories rather than in their proper MEG category - Aromatic Hydrocarbons.

TABLE 44

LRMS REPORT

SAMPLE: 2 Inlet Fraction 1

Major Categories

Intensity	Category	MW Range
100	Aliphatic hydrocarbons	up to 500

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Alkanes	254 to 504	$C_{18}H_{38}$ - $C_{36}H_{72}$
10	Alkanes	Up to 500	Up to $C_{35}H_{70}$

Other

TABLE 45

LRMS REPORT

SAMPLE: 2 Inlet Fraction 2

Major Categories

Intensity	Category	MW Range
100	Fused alternate, non-alternate hydrocarbons	<216
100	Fused alternate, non-alternate hydrocarbons	>216

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Naphthalene	128	$C_{10}H_8$
100	Alkyl Naphthalenes	142-156	$C_{11}H_{10}$-$C_{12}H_{12}$
100	Anthracene/Phenanthrene	178	$C_{14}H_{10}$
100	Alkyl Anthracene/Phenanthrene	192-290	$C_{15}H_{12}$-$C_{22}H_{26}$
* 100	Alkyl Biphenyl	196-224	$C_{15}H_{16}$-$C_{17}H_{20}$
100	Meth Fluorene	180	$C_{14}H_{12}$
10	Alkyl Pyrene/Fluoranthene	216-272	$C_{17}H_{12}$-$C_{21}H_{20}$
	Biphenylene	152	$C_{12}H_8$

Other

10 (each) Other alkylated polycyclics, m/e 218 to >300

*See Table 44

TABLE 46

LRMS REPORT

SAMPLE: 2 Inlet Fraction 3

Major Categories

Intensity	Category	MW Range
100	Fused alternate, non-alternate hydrocarbons	<216
10	Fused alternate, non-alternate hydrocarbons	>216
10	Unidentified	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Naphthalene	128	$C_{10}H_8$
100	Alkyl Naphthalenes	142-170	$C_{11}H_{10}$-$C_{13}H_{14}$
* 10	Alkyl Biphenyls	168-196	$C_{13}H_{12}$-$C_{15}H_{16}$
10	Anthracene/Phenantrene	178	$C_{14}H_{10}$
10	Alkyl Anthracene/Phenanthrene	192-234	$C_{15}H_{12}$-$C_{18}H_{18}$
10	Alkyl Pyrenes/Fluoranthenes	216-258	$C_{17}H_{12}$-$C_{20}H_{18}$

Other

10	Unidentified material at m/e 135, 149
1 (each)	Other alkylated PAH to m/e 400

*See Table 44

TABLE 47

LRMS REPORT

SAMPLE: 2 Inlet Fraction 4

Major Categories

Intensity	Category	MW Range
100	Fused alternate, non-alternate hydrocarbons	<216
100	Fused alternate, non-alternate hydrocarbons	>216
100	Heterocyclic nitrogen compounds	167-259
100	Esters	
10	Unclassified	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Carbazoles & Alkyl Carbozoles	167-233	$C_{12}H_9N-C_{16}H_{17}N$
100	Methyl Fluorenes	180-236	$C_{14}H_{12}-C_{19}H_{20}$
100	Alkyl Pyrenes/Fluoranthenes	230-286	$C_{18}H_{14}-C_{22}H_{20}$
100	Benzocarbazole & Alkylations	217-259	$C_{16}H_{11}N-C_{20}H_{17}N$
100	Phthalates		

Other

10 (each) Many other unclassified polycyclic compounds, m/e 200 to m/e 400

TABLE 48

LRMS REPORT

SAMPLE: 2 Inlet Fraction 5

Major Categories

Intensity	Category	MW Range
100	Esters	390
10	Fused alternate, non-alternate hydrocarbons	<216
10	Fused alternate, non-alternate hydrocarbons	>216
10	Heterocyclic nitrogen compounds	167-273
10	Unclassified	<360

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Phthalate, Dioctyl	390	$C_{24}H_{38}O_4$
10	Carbazole Series	167-223	$C_{12}H_9N$-$C_{16}H_{17}N$
10	Anthracene Series	178-276	$C_{14}H_{10}$-$C_{21}H_{24}$
10	Alkyl Biphenyls	196-252	$C_{15}H_{16}$-$C_{19}H_{24}$
10	Pyrene Series	202-314	$C_{16}H_{10}$-$C_{24}H_{24}$
10	Benzocarbozole Series	231-273	$C_{17}H_{13}N$-$C_{21}H_{19}N$

Other

10 (each) Unclassified alkylated polycyclics, up to m/e 360

TABLE 49

LRMS REPORT

SAMPLE: 2 Inlet Fraction 6

Major Categories

Intensity	Category	MW Range
100	Esters	390
100	Phenols	94-198
10	Heterocyclic nitrogen compounds	195-251
10	Unclassified	196-302

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Phthalate, Dioctyl	390	$C_{24}H_{38}O_4$
10	Phenol and Alkyl Phenols	94-136	C_6H_6O-$C_9H_{12}O$
10	Alkyl Biphenols	170-198	$C_{12}H_{10}O$-$C_{14}H_{14}O$
10	Naphthenol Series	144-172	$C_{10}H_8O$-$C_{12}H_{12}O$
10	Alkyl Carbazoles	209-251	$C_{15}H_{15}N$-$C_{18}H_{21}N$

Other

10	Alkylated series, m/e 196-224, probable comp. $C_{14}H_{12}O$ to $C_{16}H_{16}O$
10	Unidentified alkylated series, m/e 232, 246, 260, 274, 288, 302

TABLE 50

LRMS REPORT

SAMPLE: 2 Inlet Fraction 7

Major Categories

Intensity	Category	MW Range
100	Esters	278-290
100	Phenols	220
10	Heterocyclic nitrogen compounds	195-237
1	Unclassified	<275

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Dibutyl Phthalate	278	$C_{16}H_{22}O_4$
100	Nonyl Phenol	220	$C_{15}H_{24}O$
10	Alkyl Carbazoles	195-237	$C_{14}H_{13}N$-$C_{17}H_{19}N$
10	Dioctyl Phthalate	390	$C_{24}H_{38}O_4$

Other

1	Other possible alkylated phenols, m/e 234, 248
1	Unidentified alkylated series, m/e 232, 246, 260, 274

The heterocyclic nitrogen category was flagged by Level 1 using the worst case DMEG criterion. Examination of Level 1 reports (Table 47 through 50) shows that 16 mg/m^3 of this class are due to carbazoles and the remainder (4 mg/m^3) is due to benzocarbazoles. The worst case DMEG value for the carbazoles is 23 mg/m^3 and for the benzocarbazoles is 19 mg/m^3. Since the Level 1 amounts for these species are lower than the appropriate DMEG levels, no further effort, i.e., Level 2 analysis, is indicated.

Examination of the Level 1 data for MEG Categories 21 and 22 show that a Level 2 analysis for these categories must be undertaken. The compounds which cause these categories to be flagged, phehanthrene for the fused aromatic hydrocarbons with molecular weights less than 216 and benzo(a)pyrene for the fused aromatic hydrocarbons with molecular weights greater than 216, may be present and thus these categories may not be eliminated from consideration for further work.

The phenols identified by the Level 1 analysis are phenol, naphthol, biphenols and their alkyl substituents. The worst case DMEG value for the alkyl phenols is 10 mg/m^3 for the cresols. The level of alkyl phenols identified by Level 1, 32 mg/m^3, exceeds this value. The level of naphthols identifed by Level 1 is lower than the worst case DMEG value for that series of compounds (109 mg/m^3) and no DMEG values are available for the biphenyls. Thus, a Level 2 analysis for phenols would focus on the alkyl phenols with, at most, minor effort directed at the biphenols and the naphthols.

For the purposes of this report, the analysis of the chromatographable portion of the fused aromatic hydrocarbon and the phenols categories was undertaken to illustrate the application of Level 2 procedures to a real sample. Recommended Level 2 GC/MS procedures, using a SP 1240 DA column for phenols analysis and an OV-17 capillary column for PAH analysis, were selected from the methods in Section IV. No Level 2 sampling was performed for these illustrative examples. The reader is referred to the EPA/IERL document on the Level 2 Sampling and Analysis of Organic Materials[1] for information concerning Level 2 sampling.

C. Analysis of Phenols - Method A

Table 42 lists phenols as one of the major constituents identified by Level 1 analysis of this sample. Tables 43 through 50 show that the phenols appear in the more polar LC fractions in the coal preheater sample under examination, with a reported total phenols level of 116 mg/m^3 of which 25.5 mg/m^3 are due to TCO range material. A directed Level 2 analysis for phenols, using an optimized procedure for this category (Section IV), was performed on the combined LC fractions 5, 6 and 7. Confirmation techniques were used for both qualitative identification and quantitative results. All analyses were restricted to the phenols compound categories (MEG 18, 19 and 20).

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The approach used was as follows:

1. Analysis. The combined LC 5, 6, 7 fractions were analyzed according to the Level 2 GC/MS procedure for phenols (see Table 51). Phenols were searched for with specific emphasis on the subcategories and specific compounds flagged in the Level 1 survey. Initial tentative identifications were based on spectral matching and relative retention time data from the literature.

2. Qualitative Confirmation. A standard mixture was made containing as many of the tentatively identified phenols as were available. This mix was spiked into the combined extract and confirmation of identification was by co-chromatographing of species.

3. Quantitative Determination. Calibration mixtures containing several phenols of different types (chlorinated, alkylated, and nitro) were used to establish response curves. This calibration mixture was spiked into the combined extract to determine percent recoveries from the extract, with subsequent adjustment of concentration values obtained from the response curves as needed.

The experimental conditions used for the ^analysis of analysis of phenols are outlined in Table 51. The GC temperature program is a slight variation on the recommended conditions (85°C for 4 minutes to 200°C at 10°C/min). This change was incorporated to enhance the resolution of the more volatile components in the sample.

Figure 37 is the total ion plot for the coal preheater sample, with the peaks identified as phenols labelled. Initial examination of the sample involved the reconstruction of single-ion chromatograms for the molecular ions of phenol, alkylated phenols, chlorinated phenols, and nitrophenols, as well as the species reported as subcategories and specific compounds in the Level 1 LRMS report, namely biphenols (phenyl phenols), naphthols, and nonyl phenol (see Tables 45 and 50). Mass spectral matches were used to make initial tentative identifications.

As the labelled chromatogram shows, the major phenolic constituents identified are phenol and alkyl phenols (C_1, C_2, C_3 - alkylations), phenyl phenols, and naphthols. These TCO range components were also specified in the Level 1 report, thus illustrating excellent qualitative agreement between Level 1 and Level 2. The GRAV range phenol, nonyl phenol, will not chromatograph with the experimental conditions outlined in Table 51. In a complete Level 2 analysis, values for the GRAV range phenols would be obtained with further analytical work such as the use of the HPLC method discussed in Section IV. Chapter

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TABLE 51

Gas Chromatography and Mass Spectrometry Conditions

GC Conditions

GC:	Finnigan Model 9610
Column:	6 ft x 2 mm ID glass packed with 1% SP 1240 DA on 100/120 mesh Supelcoport
Carrier Gas:	Helium, 30 mL/min.
GC Temperature Program:	30°C isothermal for 3 min. 30-85°C rapid heating rate (∿25°C/min.) 85-200°C linear heating rate (∿20°C/min.) 200°C isothermal for 15 min.
Sample Size:	2 μL injection
Internal Standard:	d_{10}-Anthracene

MS Conditions

MS:	Finnigan Model 4000
Data System:	Finnigan Model 6110
Multiplier Voltage:	2000 V
Ionizing Energy:	60 eV
Filament Current:	0.5 amp.
Mass Range:	27-280 (excluding air interferences at m/z 28, 32, and 40)
Scan Rate:	2 sec./scan

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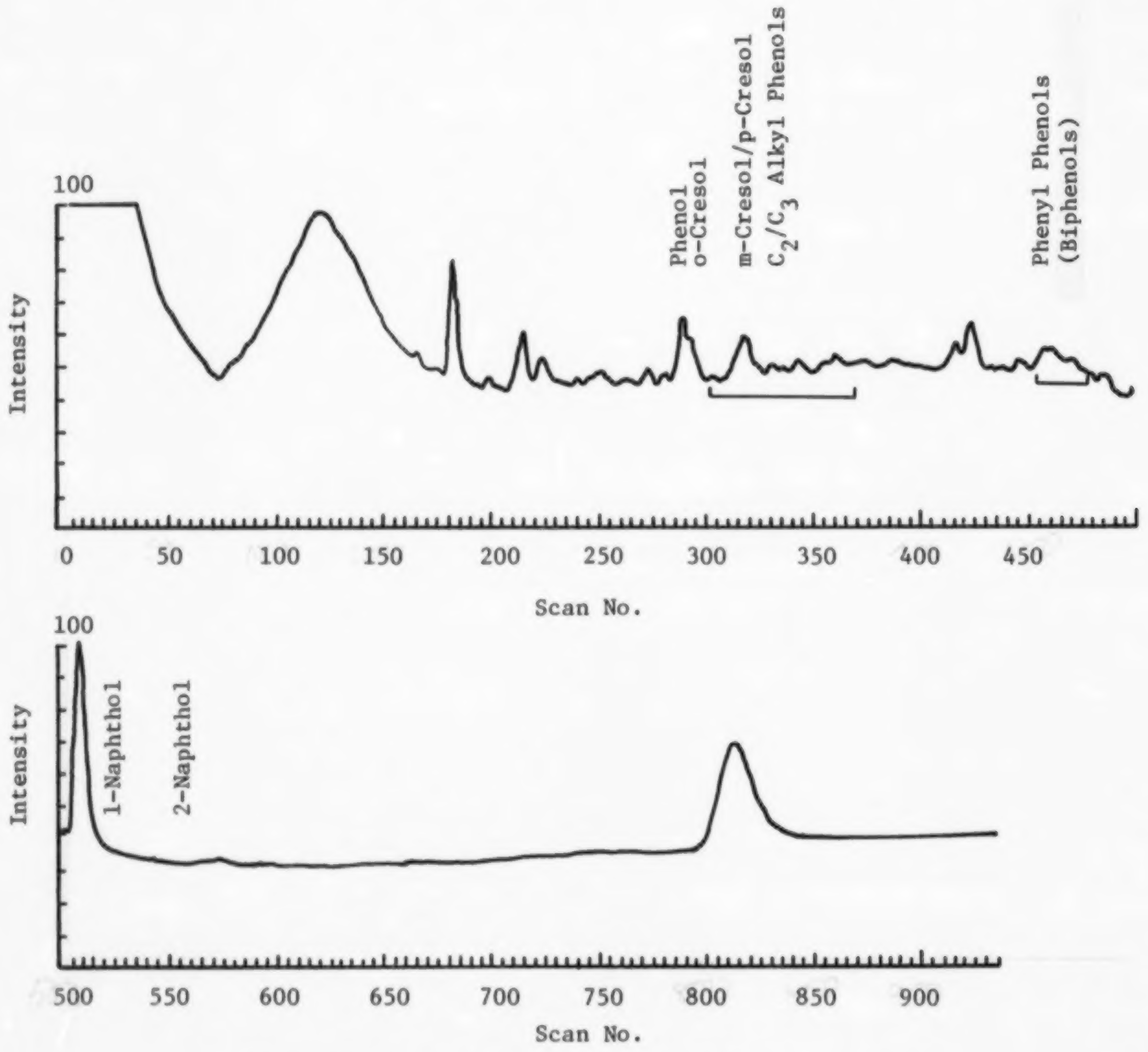

Figure 37. Total Ion Plot of Coal Preheater Sample.

To confirm the identifications of these phenols, a standard addition mixture was spiked into an aliquot of the sample, i.e., fraction 5, 6, 7 combined, and run under the same conditions. Confirmation of identification of sample component was based on exact coelution of the spiked compounds of the tentatively identified peaks. In all cases, the spiked phenols co-chromatographed with all of the respective tentatively identified peaks in the sample. The four C_2-alkylated phenols coincided with four of the m/z 122 peaks, spanning the retention time range of the tentatively identified C_2-alkylated phenols. The two C_3-alkylated phenols eluted on either end of the retention time region containing the tentatively identified m/z 136 C_3-alkylated phenols, thus confirming that retention window. Phenols, cresols, o-phenyl phenol and napthols all coincided with the previously identified sample peaks. The labelled total ion plot for the spiked sample is presented in Figure 38.

The methods used for quantitation of the identified phenols encompass a range of calibration procedures which might be used by the analyst. One method for calibration is to prepare a series of reference standards which are run under the same conditions as the sample. The response of the sample (either the raw area or the area ratio compared to an internal standard) is compared to that of the standards to obtain a concentration value. A second calibration method involves the use of a standard addition spike to the sample. Standard additions may be made at one or several levels. Concentrations are computed with the assumption that the detected response increases linearly with the amount of each constituent present in the spiked sample. Other calibration methods must be used if no reference material of the identified compound is available for use in standards. This might occur if a different isomer is available as a reference material than the compound identified or if a series of alkyl substituted materials is present in the sample while only the unsubstituted material is available as a reference material. In the former case, the calibration responses for the isomers are presumed to be equal.

For some Level 2 studies, it may be important to show whether or not the effluent source under study is perturbing the analytical results by adsorption onto non-extractable materials, for example. A spike recovery sample may then be in order to ascertain what, if any, losses occur to the sample during sample preparation and analysis. To illustrate this point, an aliquot of the sample extract was spiked to a level of 5 μg/mL and rerun with the same conditions as the previous sample. Concentrations for the spiked compounds were obtained as before and the percentage recovery calculated. The recoveries for the various phenols are shown in Table 52. Since the calibration response for the unsubstituted compound is used for the substituted compounds, the analyst must recognize that the concentrations thus obtained will be biased low. Table 52 shows the levels of the various phenols identified in this sample determined through the use of previously described calibration methods.

The quantitative data shown in Table 53 may be refined to more accurately depict the levels present in the sample by consideration of effects

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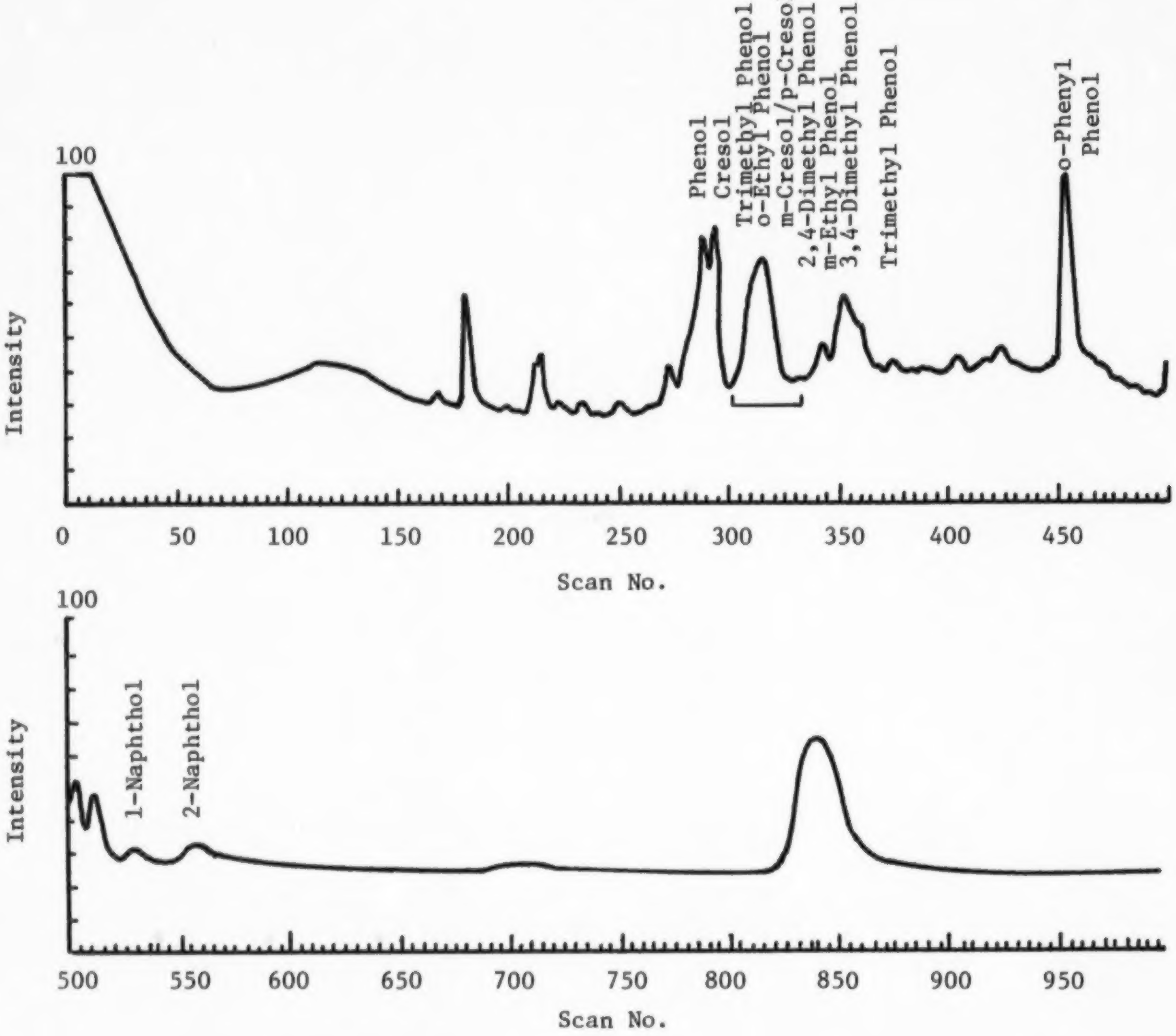

Figure 38. Total Ion Plot of Coal Preheater Sample Spiked with Standard Addition Mix

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TABLE 52

Level 2 Quantitative Data for Coal Preheater Sample - Phenols

Compound[1]	Molecular[2] ion	Conc. (mg/m^3)	Cal. Method[3]
Phenol	94	5	a
o-Cresol	108	2	b
m-Cresols and p-Cresols	108	2	b
C_2-Alkylated Phenols (5)	122	2	a,b,d
C_3-Alkylated Phenols (5-8)	136	1	b,d
Phenyl Phenols (3) (may include some alkylated naphthaldehyde components)	170	3	b,d
Methyl Phenyl Phenols (5-6)	184	2	c,d (phenyl phenol)
C_2-Alkylated Phenyl Phenols (3-7)	198	1	c,d (phenyl phenol)
1-Naphthol	144	trace	a
2-Naphthol	144	1	b
Methyl Naphthols (3)	158	1	c,d (2-naphthol)
Total		20	

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[1] Numbers in parentheses are minimum number of isomers seen.

[2] Molecular ion is analytical ion.

[3] Calibration methods used:

a. Three-point calibration from calibration mixes.
b. One-point calibration from standard addition spiking mix.
c. Used calibration data of compound in parentheses, assuming a similar structural response (e.g., all alkylated series compounds show the same response as with the unsubstituted compound).
d. Individual compounds quantified, then summed.

show
same response
as the unsubstituted
compound

53

TABLE 53

Level 2 - 2A Inlet Stack Sample Extracts LC 5,6,7 and Cal Spike

1% SP 1240 DA GC/MS

MEG Category		Percent Recovery
No.	Name	From Inlet Stack Sample Extract
18,19,20	Phenols	
	2-Chlorophenol	75%
	2-Nitrophenol	56%
	Phenol	*
	2-Ethyl Phenol	109%
	2,4-Dimethylphenol	95%
	2,4-Dichlorophenol	44%
	3,4-Dimethylphenol	107%
	2,4,6-Trichlorophenol	50%
	p-Methoxyphenol	100%

*225% measured, however, the spike level was too small compared to the level in the sample to give accurate results.

associated with the sample matrix. The recoveries for phenol and the alkyl phenols are essentially 100%, hence no adjustment due to matrix effects needs to be made to those compounds. For the chloro and nitro phenols, however, recoveries are significantly lower than 100%, ranging from 44 to 75%. For such compounds, if present in the sample, the Level 2 reported concentrations should be adjusted by the recovery value to more accurately represent the effluent discharge levels.

In addition to the qualitative agreement between the Level 1 identified phenols and the Level 2 confirmed phenols, the quantitative agreement between the two methods is very good. The Level 2 phenols analysis accounts for 20 mg/m^3 of material while the Level 1 data indicates a level of 26 mg/m^3 of phenols (TCO), i.e., Level 2 accounts for 78% of the chromatographable phenols. In addition, the only phenol identified by Level 1 in fraction 7, nonyl phenol, will not chromatograph under the conditions listed previously. If the TCO contribution from nonyl phenol is eliminated (6.2 mg/m^3), then the Level 2 and Level 1 identified phenols show excellent agreement, 20 mg/m^3 vs. 20 mg/m^3, respectively.

With the good agreement between the Level 1 and Level 2 data, the need for more extensive analysis of the coal preheater is not warranted for this illustration. If the program requirements for which this sample was being analyzed required examination of the non-chromatographable phenols, other methods, such as HPLC or high resolution probe MS, would be applied to the sample to allow analysis of the non-TCO phenols.

Once the Level 2 data has been obtained for an environmental sample, the constituents which have been quantified are compared to the DMEG values for those compounds to determine the discharge severity of the effluent being tested. Table 54 lists the concentrations, the DMEG values and the calculated discharge severity for the phenols quantified during the Level 2 study. For this sample, none of the identified phenols exceeds their respective DMEG values, a fact which would not be apparent from the Level 1 data.

D. Analysis of PAH (Method B)

The Level 1 information listed in Tables 42 through 50 show that the coal preheater sample under examination contains a substantial amount of PAH[1] which is divided about equally between TCO and GRAV range materials. A total of 180 mg/m^3 of TCO range PAH with MW ≤ 216 and 160 mg/m^3 of TCO range PAH with MW >216 is found in LC fractions 2, 3 and 4 (a minor amount of TOC range PAH [1.7 mg/m^3] is found in LC fraction 5). To illustrate a slightly different approach to Level 2 analysis than was presented for the phenol category, the analysis of combined LC fractions 2, 3 and 4 for PAH will be described.

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[1] For the purposes of this section, PAH will be defined as MEG Categories 21 and 22.

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TABLE 54

Computation of Discharge Severity for Phenols Category

Compound	Conc. (mg/m^3)	DMEG (mg/m^3)	D.S.[1]
Phenol	5	19	0.26
o-Cresol	2	22	0.09
m-Cresols and p-Cresols	2	22	0.09
C_2-Alkylated Phenols (5)	2	13	0.15
C_3-Alkylated Phenols (5-8)	1	15	0.06
Phenyl Phenols (3) (may include some alkylated naphthaldehyde components)	3	-	-
Methyl Phenyl Phenols (5-6)	2	-	-
C_2-Alkylated Phenyl Phenols (3-7)	1	-	-
1-Naphthol	trace	120	0.00
2-Naphthol	1	110	0.01
Methyl Naphthols (3)	1	-	-
TOTAL	20		0.66

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[1] D.S. = discharge severity = $\frac{\text{Conc}}{\text{DMEG}}$[54] Ref.

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The approach that was followed in this example of a partial Level 2 study is summarized below:

1. An external calibration mixture containing a number of unsubstituted PAH was used to establish a response curve for those specific PAH and the retention time of those PAH relative to an internal standard.

2. Identification of the PAH components of the sample was based on spectral matching and relative retention time information from the literature.

3. The GC separation was made on capillary GC columns to improve the resolution of individual sample components and, hence, the quality of the component identification.

The experimental conditions utilized for the PAH analysis work are presented in Table 55. These conditions were chosen to provide optimal separation of the PAH compounds containing two or more rings, while maintaining a reasonable analysis time*. The data collected from the GC/MS run of this sample were examined in detail for PAH. This examination took several forms. The specific PAH compounds identified by Level 1, such as naphthalene and its C_1 and C_2 alkyl substitutions or anthracene and its C_1 to C_8 alkyl substitutions, were searched for in the sample using selected ion chromatograms for the molecular ion of each compound under study. In addition, the data were searched for other unsubstituted PAH, such as benzo(a)pyrene, which are normally associated with combustion effluents. If these were found, their C_1 to C_4 alkyl substitutions were also sought. Finally, all of the chromatographic peaks present in the sample total ion chromatogram were examined to ensure that any other identifiable PAH would be found.

The presence of the appropriate molecular ion for any of the species of interest was not considered sufficient for identification. The spectra containing the appropriate molecular ion had to match spectra for such compounds previously obtained on the GC/MS system used for this study or to match spectra from literature sources, such as the Eight Peak Index[55], the NBS Library[56] or the Cornu and Massot Compilation[57]. In addition, the relative retention times of the tentatively identified compounds had to be consistent with literature values before an identification was presumed to be correct.

Ref.

Quantification of the identified components was based on the area of the component's molecular ion relative to that for the internal standard. Calibration mixtures of a series of unsubstituted PAH compounds was prepared at levels spanning the dynamic range of the GC/MS system. The response factors determined from the calibration mixture data were used directly for those compounds present in the calibration mixtures. To

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*These conditions correspond to one of the alternative methods for PAH listed in Section IV.

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TABLE 55

Instrumental Conditions for PAH Analysis

GC Conditions

GC:	Finnigan Model 9610
Column:	OV-17 glass capillary - 25 meter
Injection:	Grob type, splitless injection
GC Temp Program:	35°C isothermal for 1 min. 35-200°C linear heating rate at 20°C per min. 200-285°C linear heating rate at 3°C per min. 285°C isothermal operation for 45 min.
Carrier Gas:	Hydrogen, 2 mL/min. flow rate at 35°C
Sample Size	2 μL injection
Internal Standard:	d_{10}-Anthracene

MS Conditions

MS:	Finnigan Model 4000
Data System	Incos Model 2300
Multiplier Voltage:	1600 V
Ionizing Energy:	50 ev
Filament Current:	40 mA
Mass Range:	125-310 amu
Scan Rate:	2 sec./scan

55

TABLE 55

Instrumental Conditions for PAH Analysis

GC Conditions

GC:	Finnigan Model 9610
Column:	OV-17 glass capillary - 25 meter
Injection:	Grob type, splitless injection
GC Temp Program:	35°C isothermal for 1 min. 35-200°C linear heating rate at 20°C per min. 200-285°C linear heating rate at 3°C per min. 285°C isothermal operation for 45 min.
Carrier Gas:	Hydrogen, 2 mL/min. flow rate at 35°C
Sample Size	2 μL injection
Internal Standard:	d_{10}-Anthracene

MS Conditions

MS:	Finnigan Model 4000
Data System	Incos Model 2300
Multiplier Voltage:	1600 V
Ionizing Energy:	50 ev
Filament Current:	40 mA
Mass Range:	125-310 amu
Scan Rate:	2 sec./scan

estimate the levels of alkyl substituted PAH present in this sample, the same response factors were assumed for both the unsubstituted and the alkyl substituted PAH species. However, this method for quantifying the alkyl substituted PAH tends to underestimate their levels as compared to direct calibration against appropriate standards. The PAH species identified and their corresponding levels are tabulated in Table 56. For comparative purposes, all values have been computed in terms of mg/m^3.

Comparison of the data obtained for PAH between the Level 1 report and this partial Level 2 analysis show several interesting facts. All of the specific compounds and subcategories reported with an intensity level of 100 by Level 1 are identified with the Level 2 approach used. Although the Level 2 procedure identifies only 39% of the Level 1 implied TCO range material (133 mg/m^3 out of 340 mg/m^3), the amount reported by molecular weight range (i.e., MW ≤ 216 and MW >216) show large differences. The lower molecular weight range is fairly well accounted for by this partial Level 2 analysis (110 mg/m^3 out of 183 mg/m^3 or 60% accounted for), while the higher molecular weight range has only 14% of its Level 1 amount accounted for by this Level 2 method. If this sample were being analyzed as part of a complete Level 2 study, a number of actions would be taken to determine the source of the low results obtained above. These actions might include reanalyzing the sample for TCO range materials with different GC and MS conditions to provide better separation of the compounds, analyzing a larger aliquot or a concentrated aliquot of the sample by GC/MS to enhance the detection and identification of low level components which might be missed in the background noise, HPLC methods such as those discussed in Chapter IV or through the use of probe MS for the less volatile organics. For this example, no further actions were taken, but the possible reasons for the low results offer insight into some of the analysis considerations pertinent to a Level 2 study.

Several reasons which help to explain, at least in part, the low results for the PAH category are presented in the following:

1. The purpose of Level 1 is to give semiquantitative estimates of compound classes within a factor of 3. The TCO and GRAV measurements which are more accurate than a factor of 3 are partitioned between those reporting categories identified by IR and LRMS. IR identifies the presence of both saturated and unsaturated hydrocarbons in the LC fractions tested, but is unable to differentiate between aliphatics and long chain alkyl substituted PAH in these complex mixtures. LRMS may lose the light end components during sample drydown for the probe analysis. Any aliphatic hydrocarbons which were carried over into LC fraction 2 may be lost during drydown and thus not identified when in the presence of higher levels of PAH material. However, the TCO value for such compounds would be incorporated into the identified

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TABLE 56

PAH Data for Coal Preheater Sample

	Compound/Composition/mz	Conc. (mg/m^3)
*	Naphthalene/$C_{12}H_{10}$/128	10
**	Methyl naphthalenes/$C_{11}H_{10}$/142	9.9
**	Dimethyl naphthalenes/$C_{12}H_{12}$/156	12
**	Trimethyl naphthalenes/$C_{13}H_{14}$/170	8.7
**	Tetramethyl naphthalenes/$C_{14}H_{16}$/184	5
	Biphenyl, etc./$C_{12}H_{10}$/154	8.7
	Methyl biphenyl/C_3H_{12}/168	4.6
	Dimethyl biphenyl/$C_{14}H_{14}$/182	3.3
	Trimethyl biphenyl/$C_{15}H_{16}$196	21
	Tetramethyl biphenyl/$C_{16}H_{18}$/210	0.4
	Terephenyl/$C_{18}H_{14}$/230	6.4
*	Fluorene/$C_{13}H_{10}$/166	1.1
**	Methyl fluorene/$C_{14}H_{12}$/180	1.7
**	Dimethyl fluorene/$C_{15}H_{14}$/194	0.9
*	Anthracene/phenanthrene/$C_{14}H_{10}$/178	6.4
**	Methyl anthracenes, etc./$C_{15}H_{12}$/192	6.8
**	Dimethyl anthracenes, etc./$C_{16}H_{14}$/206	4.7
	$C_{16}H_{12}$-Phenylnaphthalene/$C_{16}H_{12}$/204	1.9
*	Fluoranthene/$C_{16}H_{10}$/202	0.6
*	Pyrene/$C_{16}H_{10}$/202	0.5
**	Methylpyrenes, etc./$C_{17}H_{12}$/216	1.7
**	Trimethyl anthracenes, etc./$C_{17}H_{16}$/220	2.3
**	Tetramethyl anthracenes, etc./$C_{18}H_{18}$/234	0.5
	Methyl C_6H_{12}(phenyl naphthalene)/$C_{17}H_{14}$/232	2.3
*	Benz(a)anthracene/$C_{18}H_{12}$/228	0.4
*	Chrysene/triphenylene/$C_{18}H_{12}$/228	0.8
**	Methyl benzanthracene, etc./$C_{19}H_{14}$/242	1.2
*	Dimethyl benzanthracene, etc./$C_{20}H_{16}$/256	1.0
	Binaphthyl/$C_{20}H_{14}$/254	0.29
*	Benzofluoranthenes/$C_{20}H_{12}$/252	0.42
*	Benzo(e)pyrene/$C_{20}H_{12}$/252	0.36
*	Benzo(a)pyrene/$C_{20}H_{12}$/252	0.14
**	Methyl benzopyrenes/$C_{21}H_{14}$/266	0.8
*	Indeno(1,2,3-cd)pyrene/$C_{22}H_{12}$/276	0.02
*	Benzo(g,h,i)perylene/$C_{22}H_{12}$/276	0.06
*	Dibenzanthracenes/$C_{22}H_{14}$/278	0.02
	3-Methyl cholanthrene/$C_{21}H_{16}$/268	0.03
	Dimethyl phenyl naphthalene/$C_{18}H_{16}$/232	5.6

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* Concentration values from standard mixtures

** Concentration values estimated by use of calibration factor for unsubstituted analog (these values could be biased lower than "true" value).

Other Compounds--concentration values estimated by assuming number of ions produced for compounds and internal standards are the same for the same internal standard and compound.

✓ TCO

✓ TCO

categories (i.e., the TCO range Level 1 PAH value may be biased high).

2. TCO range materials in this sample with molecular weights less than 125 (the lower limit for the chosen analytical method), for example, benzene, indene, etc., would not be identified with the partial Level 2 analysis approach used.

3. The alkyl substituted fused aromatics (approximately 67% of the total fused aromatics found by Level 1) are subject to a negative bias in the Level 2 analysis due to the calibration procedure used. For a more extensive Level 2 effort, direct calibration procedures would be used for alkyl substituted PAH to avoid the problem of negative bias during calibration.

4. As the number of isomers increases for a component at a given molecular weight, it becomes more difficult to determine the identity of such compounds, i.e., the characteristic ions of such compounds are lost in the GC/MS system background noise. This contributes to the fact that alkyl substitutions greater than C_4, i.e., tetramethyl, etc., are not reported in the Level 2 report. In the Level 1 approach, however, the many isomers add their common signals and thus become more readily identifiable. Since only those components which could be identified by spectral match and retention time were quantified, other compounds which did not neet these two criteria, such as the higher than C_4 alkyl substituted PAH, were left out of the Level 2 mg/m^3 value.

5. The mass spectrometer used, a Finnigan 4000 quadrupole instrument, does show some discrimination against high m/z ions, which hinders the identification of the higher molecular weight polycyclic hydrocarbons seen by Level 1 during the Level 2 investigation. In addition, PAH with high molecular weights show poorer chromatography than the lighter PAH which may cause low level high molecular weight PAH to be missed.

These factors illustrate some of the cautions which must be recognized during any Level 2 study. The instrumental bias in Level 2 and in Level 1 (points 1 and 5 above) need to be considered when examining the experimental data. To investigate the possibility of light molecular weight TCO material in this sample, a different set of GC and MS conditions would be used, while LC methods might be used to clarify the levels of the higher molecular weight PAH. Any calibration method bias should be recognized by the analyst during the Level 2 study and, if appropriate, steps taken to remove that bias.

C

E. Extended Analysis of Combined Polar Fractions (Method C)

In the previous two Level 2 analysis approaches (Methods A and B), the sample was examined for only those compounds contained in the category of interest, i.e., the phenols in fractions 5, 6 and 7 or the PAH in LC fractions 2, 3 and 4. To maximize the information content obtained during a Level 2 analysis, one might perform Level 2 analyses for those major categories directed by Level 1, but during the identification and quantification phase of the Level 2 program, include information on all compounds found even though they are not members of the principal category under study. As an example, this approach was applied to the results of the GC/MS analysis of the LC 5, 6 and 7 fractions using a SP 1240 DA column. The experimental conditions used for this approach are those reported previously for the phenols. The following discussion illustrates the additional information which can be obtained concerning a sample as a by-product of Level 2 analysis for some particular compound type.

Figure 39 shows the total ion chromatogram for the coal preheater sample with the identifiable non-phenolic component peaks labeled. For clarity, those peaks which were due to phenols have been marked with an asterisk. Since one of the goals of this Level 2 approach is to maximize the sample information while minimizing cost, the examination for non-phenols included only those peaks apparent on the total ion chromatogram. The categories found in this sample other than phenols include aldehydes, esters, ketones and aromatics. The concentrations of the identified non-phenolic components are tabulated in Table 57; calibration methods for the non-phenolic components are the same as those discussed in Section C.

Tentative identification of the components listed in Table 57 was based on the mass spectra of the eluting compounds. These identifications were confirmed by either exact relative retention time matches to an external calibration mix or by coelution of the compound with the appropriate spiking solution component.

The use of confirmatory methods is especially important in the Level 2 approach as used here, since the analytical finish used was optimized for phenols and is not optimum for other compound categories. This is best illustrated by example.

During the initial qualitative analysis of the sample, a single ion chromatogram for m/z 118 showed a peak at scan 243. The mass spectrum of this peak (Figure 40a) displayed several major ions, including m/z 134, 133, 118, 105, 90 and 89. No literature match could be found for this spectrum and the ion pattern, e.g., mass differences between ions, is not consistent with normal ion fragmentation pathways for a single compound. The next step was to consider the possibility of coelution of two or more species near scan 243. Single ion chromatograms of the other major ions in the mass spectrum of Figure 40a showed m/z 118, 89 and 90 to maximize at scan 243 while m/z 134, 133, 105 and 119 at scan 241. Another mass spectrum was obtained for the scan 243 peak, this time using scan 241 for a background to eliminate the contribution from the previous eluting compound(s).

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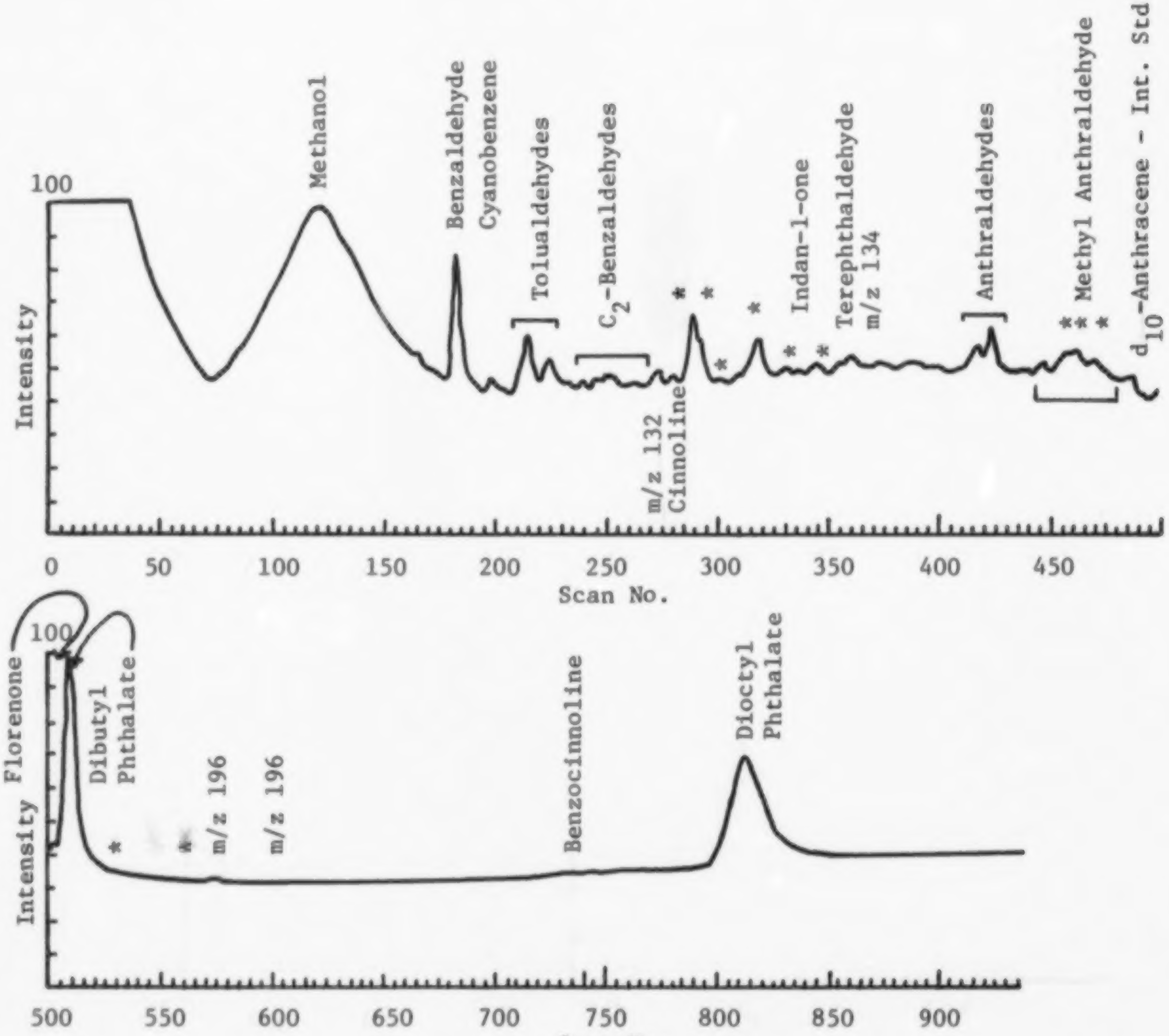

Figure 39. Total Ion Plot of Coal Preheater Sample.

TABLE 57

Quantitative Data for Coal Preheater Sample Non-phenolic Components

MEG Category	Compound[1]	Molecular Weight[2]	Concentration (mg/m^3)	Calibration Method[3]
7A Aldehydes	Benzaldehyde	106	5.0	b
	Tolualdehydes (3)	120	6.2	b
	C_2-benzaldehydes (6-8)	134	2.0	b
	C_3-benzaldehydes (8)	148	0.8	d (C_2-benzaldehyde)
	Phenyl benzaldehydes (2-3)	132	0.1	d (benzaldehyde)
	Terephthaldehyde	134	0.1	b
	Naphthaldehydes (2)	156	3.2	c
7B Ketones	Fluorenone	180	0.8	b
	Anthrone	194	-	b
	Indan-1-one	132	0.23	c
	Alkyl indanones (7-10)	146,160	trace	d (indan-1-one)
8D Esters	Dimethylphthalate	(149)	trace	a
	Dibutylphthalate	(149)	>14	c
	Dioctylphthalate	(149)	9.0	a
	Phthalic acid/anhydride	(104)	0.4	b
9 Nitriles	Benzyl cyanide	117	-	b
	Cyanobenzene	103	0.6	c
15 Aromatics	Toluene	92	0.4	c
	Xylenes (3)	106	-	c

TABLE 57 (Cont'd)

Quantitative Data for Coal Preheater Sample
Non-phenolic Components

MEG Category	Compound[1]	Molecular Weight[2]	Concentration (mg/m^3)	Calibration Method[3]
23 Heterocyclic nitrogen	Cinnoline	130	trace	c
	Benzo(c)cinnoline	180	0.4	c
	Carbazole	167	trace	a
24 Heterocyclic oxygen	Coumarin	146	trace	c
Unclassified	m/z 134, 148, 162	134,148,162	0.9	d (terephthaldehyde)
	m/z 168	168	0.7	c
	m/z 194 (4)	194	0.6	c
	m/z 196 (5)	196	0.9	c
	m/z 210 (3-6)	210	0.4	c
	m/z 184 (5)	184	0.1	c

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[1] Numbers in parentheses are minimum number of isomers seen.

[2] Molecular ion is analytical ion, except for those in parentheses, when noted that ion was used instead of molecular ion.

[3] Calibration methods used:
A) Three (3) point calibration from calibration mixes.
B) One (1) point calibration from standard addition spiking mix.

TABLE 57 (Cont'd)

Quantitative Data for Coal Preheater Sample
Non-phenolic Components

C) It was assumed that the total ion current (TIC) (summed absolute intensities for all ions in the mass spectrum of a compound) per ng of compound is a constant. Therefore, the TIC for X ng of any compound should be proportional to the TIC for a known amount of any compound, in this case, an internal standard - d_{10}-anthracene. For d_{10}, m/z 188 (the analytical ion) is ∿100% of the TIC. For any compound, compute the approximate percent of TIC for the analytical ion and set up a proportionality with the known concentration of internal standard:

$$\frac{\text{conc. IS}(2.5\ \text{ng}/\mu\text{L})}{\text{area } 188(\text{IS}) \times 100\%} = \frac{\text{concentration of compound}}{\text{area } m/z(\text{compound}) \times \text{analytical ion } \%}$$

D) Used calibration data of compound in parentheses, assuming a similar structural response (e.g., alkylated series).

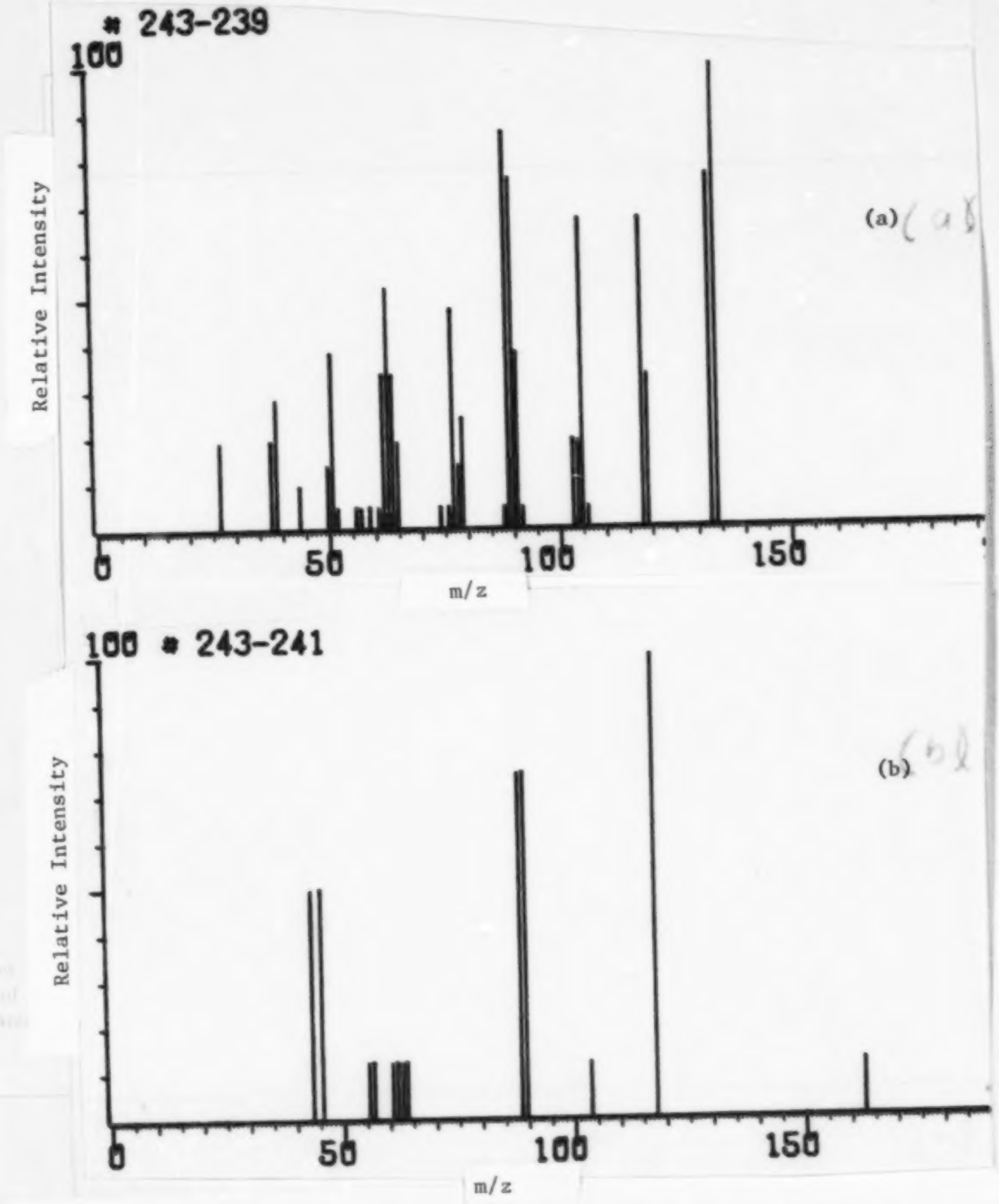

Figure 40. (a) Mass spectrum of m/z 118 peak at scan 243 from coal preheater sample run. Contains contributions from several coeluting species.

(b) Mass spectrum of m/z 118 peak at scan 243 with background subtract adjusted to eliminate contribution from coeluting specie(s) at scan 241.

39b

This mass spectrum is displayed in Figure 40b. The only literature reference for a mass spectrum with base peak at m/z 118 and next most abundant ion at m/z 89 and 90 was benzofuran. Relative intensities listed were: m/z 118 (100%), 90 (28-57%), 89 (28-52%). In the mass spectrum in Figure 40b, m/z 89 and 90 are at 75% of m/z 118. Although these are higher than the literature values, it must be kept in mind that this peak is at a very low overall intensity and low level compounds can show significant fluctuations in the relative abundances of minor ions in their mass spectra. On the basis of this, the peak was tentatively identified as benzofuran.

39b

Benzofuran was present in the standard addition spiking mix. The single-ion chromatogram for m/z 118 in the run of the coal preheater sample spiked with the standard addition mix is shown in Figure 41a. Benzofuran and the previously identified m/z 118 peak at scan 243 are clearly different, thus invalidating the earlier identification of the scan 243 peak as benzofuran. The mass spectrum of the benzofuran peak from the standard addition spike is shown in Figure 41b.

40 40a

Clearly, misinterpretations can result when several compounds coelute and/or when a peak is at a very low concentration level. Thus, special care must be taken by the analyst when identifying low level species in a complex matrix.

Several peaks were found for m/z 194 (Figure 42a). The spectra of these peaks were difficult to match well as they were all of low intensity. Nevertheless, spectral match possibilities included the methyl fluorenone isomers (fluorenone had been previously identified via a literature match for peak at scan 502, m/z 180) and anthrone.

Anthrone was included in the standard addition spiking mix. The single-ion chromatogram for m/z 194 from the run of the sample spiked with the standard addition mix (Figure 42b) shows anthrone to elute much later than the set of m/z 194 peaks. This rules out anthrone as a possible identification for any of these peaks.

The low intensity levels of these components and the absence of any methyl fluorenone in either the spiking or calibration mixtures prevents positive identification of these peaks as methyl fluorenone. Thus, none of the peaks were assigned tentative identifications. These ions are reported instead as unclassified material of m/z 194.

Two peaks were found in the ion chromatogram for m/z 134 that exhibited nearly identical mass spectra (Figure 43a & b). These spectra matched the literature reference for terephthaldehyde, but since there were two chromatographic peaks for a compound with only one isomer, positive identification as to which peak might actually be terephthaldehyde could not be made without additional information.

Terephthaldehyde was present in the standard addition spiking mix. By comparing the two single-ion chromatograms for m/z 134 in the sample

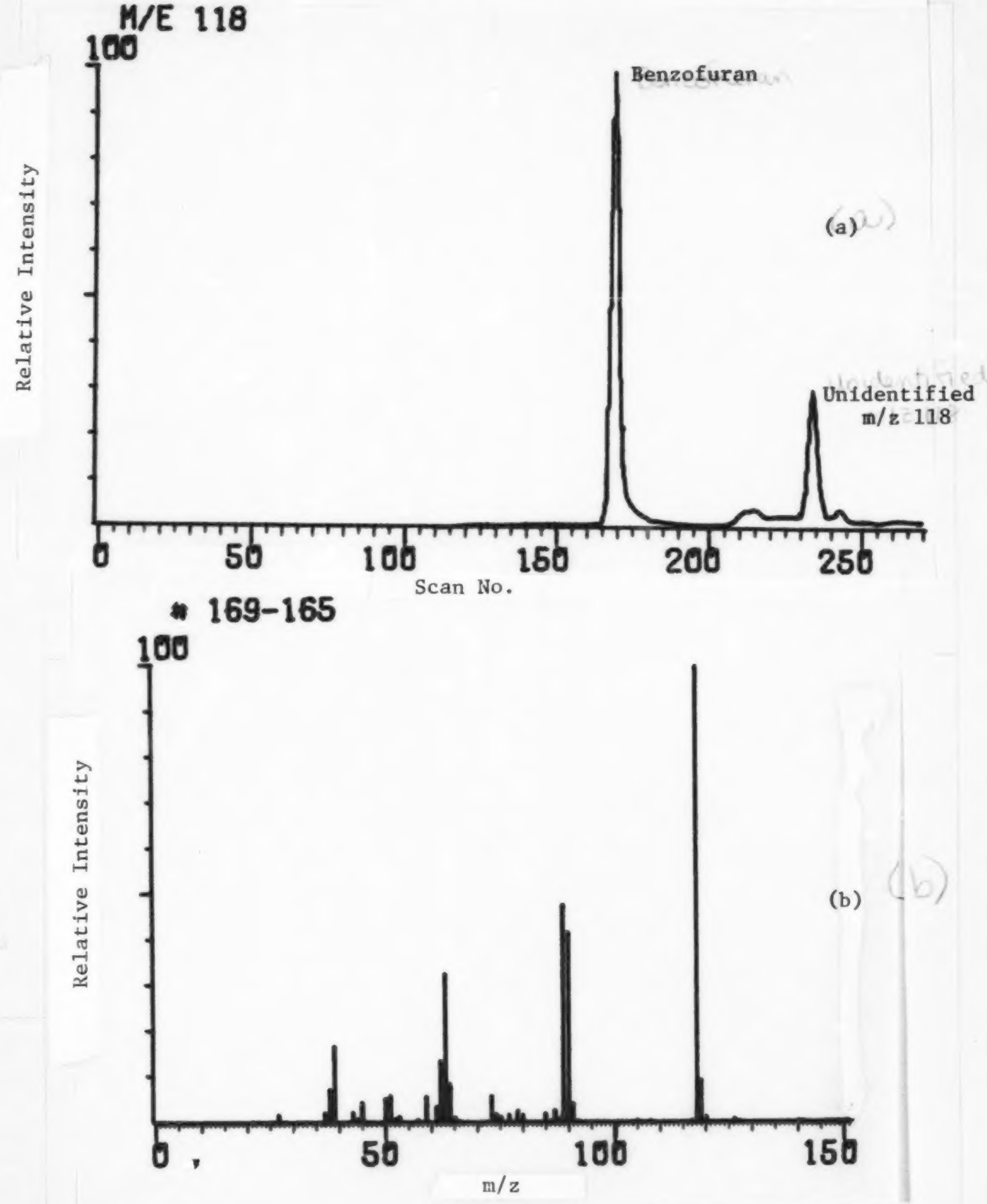

Figure 41. (a) Ion chromatogram of m/z 118 in coal preheater sample spiked with standard addition mix.

(b) Mass spectrum of benzofuran.

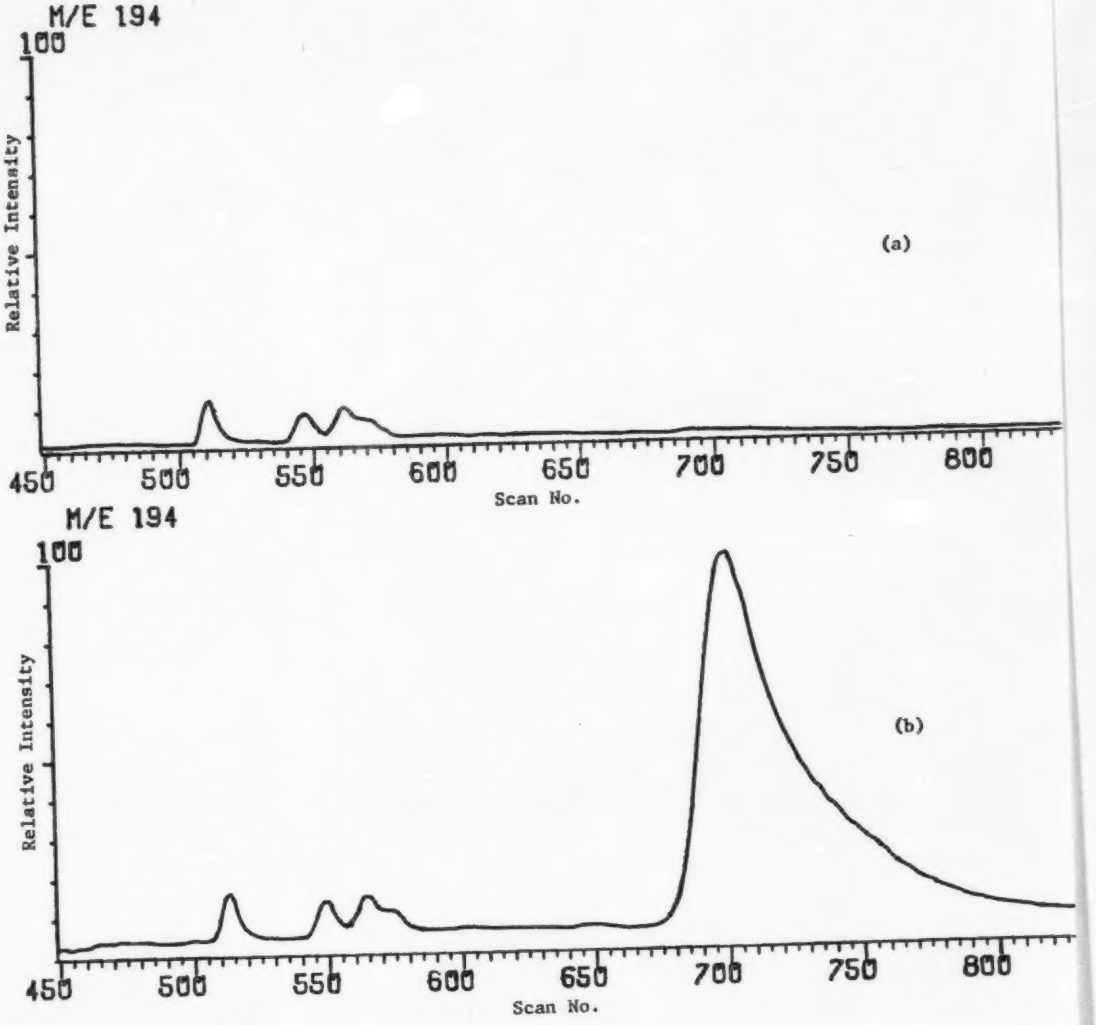

Figure 42. (a) Ion chromatogram for m/z 194 from coal preheater sample.

(b) Ion chromatogram for m/z 194 from coal preheater sample spiked with standard addition mix.

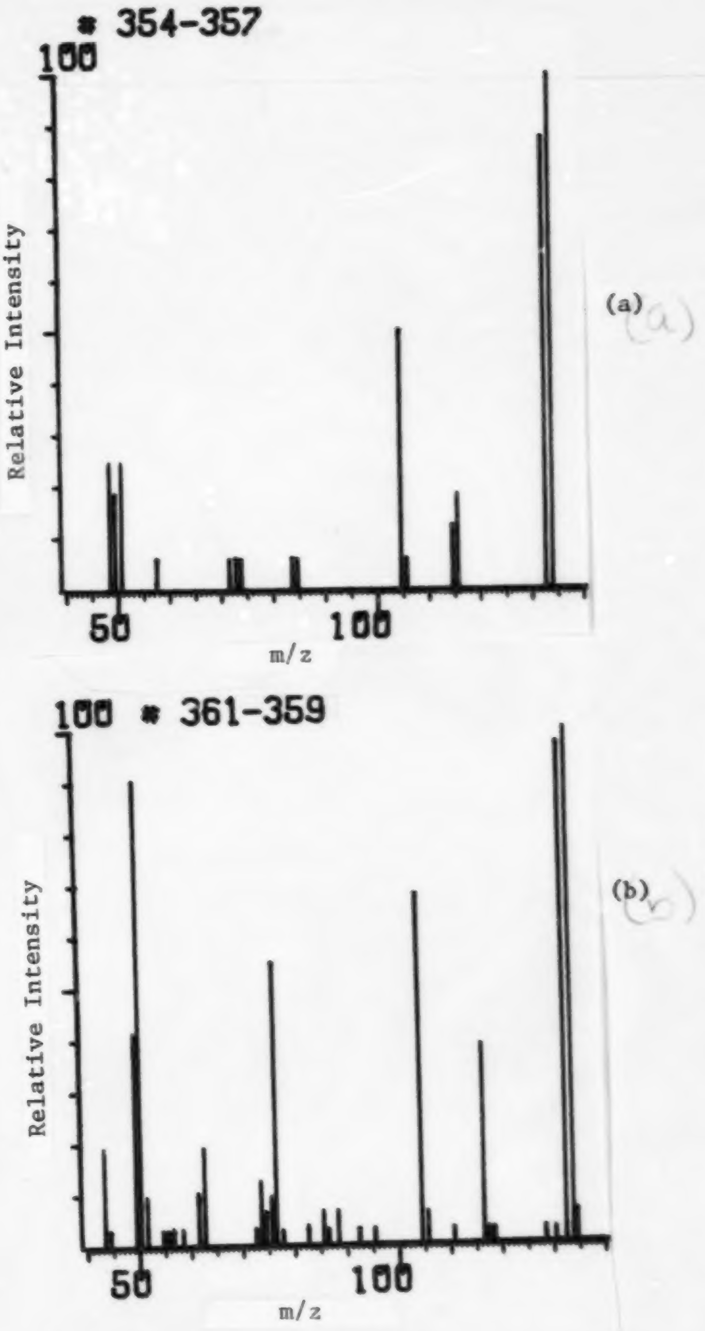

Figure 43. Mass spectra of two m/z 134 peaks in the coal preheater sample.

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alone (Figure 44a) and in the sample spiked with the standard addition mix (Figure 44b), clearly the first of these two peaks is confirmed as terephthaldehyde. The identity of the second peak was left as an unclassified compound of m/z 134, but because of the spectral and, therefore, potential structural similarities between the two, quantitation for this second peak was based on the data for terephthaldehyde.

In cases of very low level species, positive identification solely on the basis of literature spectral matches, can be misleading without some further confirmation, for instance, coelution with spiked amounts of the compounds tentatively identified or with good relative retention time and spectral matches to a calibration standard.

The use of non-optimized methods for Level 2 analyses must be pursued with care. If the recommended Level 2 methods are closely related (i.e., similar GC conditions for the same GC column), good results may be expected for the multiple categories examined. However, when the recommended GC columns and conditions are widely different, such as for phenols and aromatics or for phenols and esters, the data may be distorted. For example, the temperature limitations of the phenols GC column is too low to permit elution of PAH compounds, such as chrysene or benzo(a)pyrene. Similarly, the phthalate esters identified by Level 1 elute well after the completion of the GC/MS run under the conditions utilized for this example. Any attempt to quantify the phthalate esters or the PAH with MW >216 would be impossible using these non-optimum conditions. Also, the recoveries of the materials being examined under non-optimum conditions is highly variable as shown in Table 58. An extended analysis such as that described here, should only be used to better characterize the sample and, if warranted, the sample should be rerun using the recommended conditions for those categories of interest.

The results of this Level 2 analysis are consistent with the Level 1 reporting of this sample. Each of the major categories reported at Level 1 in LC fractions 5, 6 and 7 -- phenols, esters and heterocyclic nitrogen -- were found in one GC/MS analysis of the combined fraction sample even though the analytical conditions were optimum for phenols. The few categories of compounds found in Level 2, but not reported in Level 1, are at trace levels and would easily have been obscured by the presence of the more abundant materials identified in Level 1 and confirmed in Level 2. These materials are all TCO range compounds (batch inlet LRMS) for which the Level 1 LRMS has reduced sensitivity.

F. Summary

This section has illustrated three different approaches which might be applied during a Level 2 study. In addition, several aspects concerning the transition between Level 1 and Level 2 and the end use of the Level 2 data were described. The experimental approaches discussed for Level 2 use show good qualitative agreement between the results obtained by Level 1 and Level 2 methods. In all of these examples, the Level 1 identifications of compound class subcategories and specific compounds

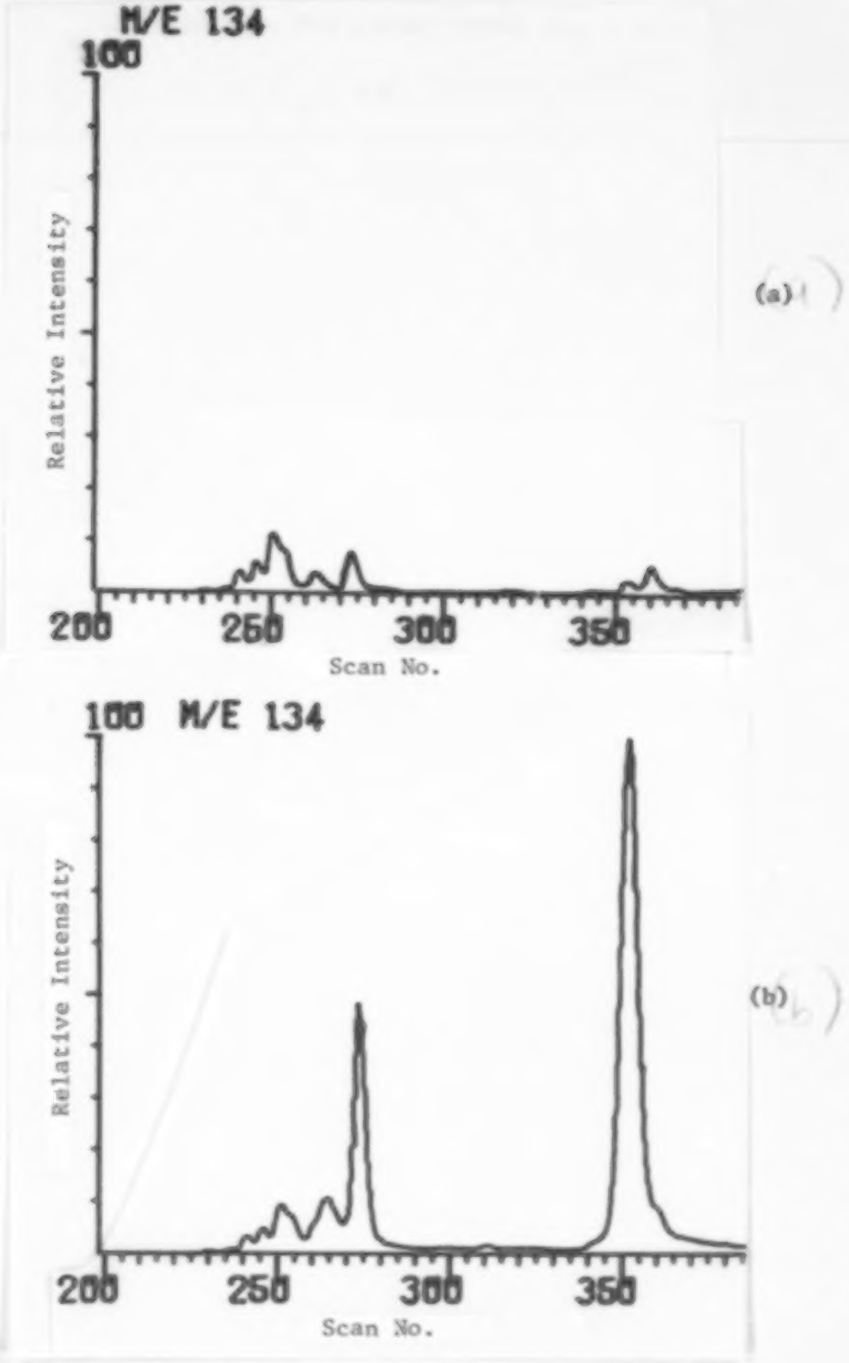

Figure 44. (a) Ion chromatogram of m/z 134 for coal preheater sample.

(b) Ion chromatogram of m/z 134 for coal preheater sample spiked with standard addition mix.

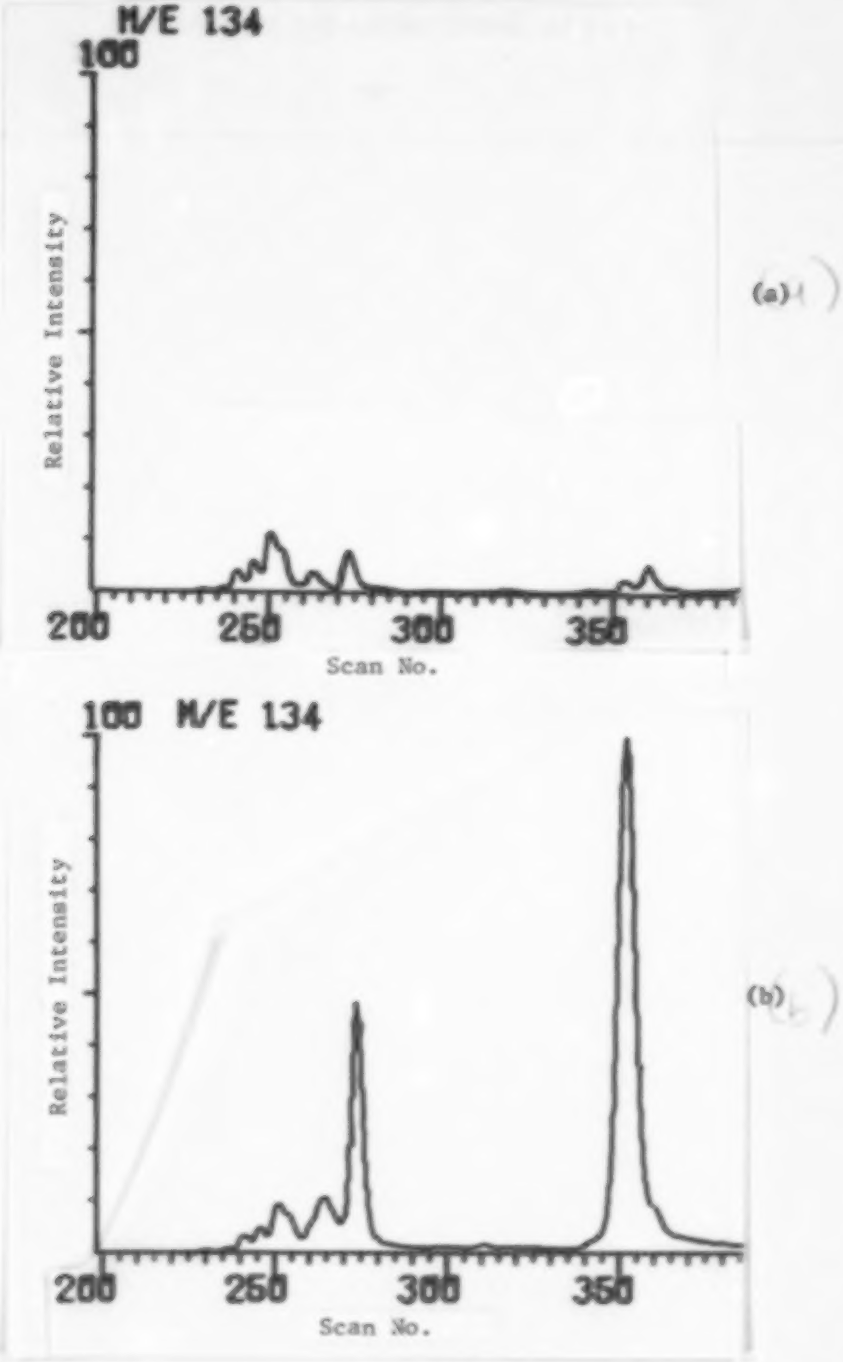

Figure 44. (a) Ion chromatogram of m/z 134 for coal preheater sample.

(b) Ion chromatogram of m/z 134 for coal preheater sample spiked with standard addition mix.

TABLE 58

Recovery Data From Level 2 Calibration Mix Spiked Into Coal Preheater Sample Extract

MEG Category	Recovery
7B Ketones	
Acetone	--
Butanone	--
2-Pentanone	--
Mesityl oxide	67
2-Methylcyclohexanone	100
3-Methylcyclohexanone	63
2-Nonanone	63
8D Esters	
Isobutyl acetate	17
Diethyl oxalate	50
Methyl benzoate	9
Methyl salicylate	129
Diethyl adipate	113
Dimethyl phthalate	--
Dioctyl phthalate	103
23 Heterocyclic Nitrogen	
Pyridine	--
Pyrrole	--
Benzothiazole	43
3-Methylindole	55
Acridine	--
Carabazole	--

were confirmed with Level 2 methods. The quantitative agreement between the Level 1 results and the Level 2 results was highly variable, ranging from excellent for the phenols to poor for the PAH with MW >216 for this sample. For the specific conditions utilized for PAH analysis, the poor quantitative agreement between the Level 1 and Level 2 results was not unexpected and serves to highlight the fact that multiple analysis methods (GC/MS, HPLC, etc.) are needed to achieve the desired characterization of a sample during Level 2 studies.

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APPENDIX A

PACKED GAS CHROMATOGRAPHY COLUMNS

Most of the analytical methods recommended for Level 2 studies use packed gas chromatography (GC) columns. The specified GC liquid phases and equivalent liquid phases are listed in Table A-1. Liquid Phases were considered equivalent when the published McReynolds constants were similar. The McReynolds constants are directly related to the retention times determined for selected test compounds representative of various categories of organics, e.g., benzene, butanol, pyridine, 1,4-dioxane. These constants may be used to select substitute liquid phases of similar selectivity. Other important criteria for selecting liquid phases include minimum and maximum operating temperatures, absolute solubility of the analyte in the liquid phase, and availability.

The solid support most frequently indicated for these Level 2 methods is Supelcoport (SP). Supelcoport is a fluxcalcined diatomaceous earth that has been acid washed and silanized using dimethyldichlorosilane. Other manufactured supports similar to Supelcoport are Chromosorb W HP, Chromosorb G HP, Gas ChromQ and AnakromQ. Carbopacks are also used as solid supports. Carbopacks are carbon blacks with surfaces graphitized using a proprietary procedure.

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TABLE A-1

Gas Chromatography Liquid Phases

Specified Liquid Phases	Description	Equivalent Liquid Phases
SP-1000	Carbowax plus substituted terephthalic acid	FFAP
SP-1240DA	Polyester deactivated with H_3PO_4	
SP-2100	100% dimethyl silicone	OV-101, DC-200, JXR silicone, SE30 (gum) OV-1 (gum)
SP-2250	50% Methyl, 50% Phenyl Silicone	OV-17
SP-2401	Silicone Trifluoropropyl	QF-1, OV-210
Carbowax 20M	Polyethylene Glycol, M.Wt. 15,000 to 20,000	
Dexsil 400	Carborane - Methyl Phenyl Silicone	

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APPENDIX B

CAPILLARY GAS CHROMATOGRAPHY COLUMNS

Capillary GC columns offer advantages to the analyst in Level 2 studies focussing on chromatographable compounds over conventional packed GC columns. The higher resolution of capillary columns aids the analyst by minimizing chromatographic interferences which may occur during a Level 2 study and by increasing the signal to noise ratio of those GC peaks which are present in the sample. The latter arises from the consideration that the detected peak area, which is nominally the same for either capillary or packed GC analyses, has been condensed into a much narrower width with capillary columns. One disadvantage of capillary columns is that their capacity is not as high as with packed GC columns.

Capillary columns may be prepared on metal, glass or fused silica surfaces. Metal surfaces tend to be highly reactive and this reactivity may severely complicate a Level 2 analysis if metal capillary GC columns are used. The remainder of this discussion will focus on the more inert glass capillary or fused silica capillary GC columns for use in Level 2 studies. Fused silica columns are somewhat more inert than glass columns and are not as fragile as glass columns, but the following discussion makes no presumption as to which type of column is being used.

The phases which are commercially available for coating on glass or fused silica capillary columns are fairly limited. For the most part, the polarity ranges between that of methyl silicone phases (low polarity) and treated polyethylene glycol phases (higher polarity). Table B-1 includes some data concerning the polarity of some typically available capillary GC column phases, i.e., the McReynolds' constants for the listed phases.

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Table B-2 lists some recommended capillary columns for Level 2 use by MEG category. One item which is not described in this table is the proper procedure for deactivation of the column (either in processing by the manufacturer or by the uses if the column ends are straightened) which can alter the performance of the column. In general, the capillary column surface is slightly acidic, especially for fused silica columns. Deactivation with Carbowax, for example, tends to make the column slightly basic. Other deactivation procedures, such as silylation or siloxation, may also be used. Typically, instructions on deactivation or capillary GC columns are available from the manufacturer and may be included with a purchased column.

For the most part, the capillary columns listed in Table B-2 parallel those described previously in Table 2 for packed column GC of the MEG categories. There also is a high degree of overlap between the possible capillary columns which may be used in Level 2 studies. Often columns coated with Carbowax 20M and with SE-30 have been used successfully for the same analyses, even though these two coatings span the polarity range available for commercial capillary columns. In general, a methyl silicone column, one coated with SP 2100 or SE-30, for example, is preferred since such a column tends to have a higher temperature range than for a Carbowax 20M coated column and is less subject to degradation from trace amounts of oxygen in the carrier gas or water in the sample than is a Carbowax 20M coated column. When the presence of water is suspected in a sample and the Level 2 analysis requires a polar column, an OV-17 coated column can frequently be substituted for a Carbowax-coated column with success.

TABLE B-1

Comparison of Capillary Column GC Phases Listed by Increasing Polarity

Phase	Description	McReynolds' Constants X'	Y'	Z'	U'	S'
SE-30, OV-1	Methyl silicone gum	15	53	44	64	41
SP 2100, OV-101	Methyl silicone liquid	17	57	45	67	43
SE-52	5% Phenyl-methyl silicone	32	72	65	98	64
SE-54	5% Phenyl, 1% vinyl methyl silicone	33	72	66	99	67
Dexsil 300	Carborane-methyl silicone	47	80	103	148	96
Dexsil 400	Carborane-methyl phenyl silicone	72	108	118	166	123
OV-17, SP 2250	50% Phenyl methyl silicone	119	158	162	243	202
Carbowax 20M	Polyglycol	322	536	368	572	510
SP 1000, FFAP	Carbowax 20M + nitroterphthalic acid	332	555	393	583	546
SP 2330, Silar 9CP	68% Cyanopropyl silicone	490	725	630	913	778

B-2

TABLE B-2

Capillary Columns for Level 2 Analysis

MEG Category	Description	Column Coating Applicable
1	Aliphatic hydrocarbons	SP 2100, SE-30
2a,b	Alkyl halides	SP 1000, Carbowax 20M, SE-30
3	Ethers	SP 1000, Carbowax 20M
4	Haloethers	SP 1000, Carbowax 20M
5	Alcohols	Carbowax 20M
6	Glycols, Epoxides	-- 1
7	Aldehydes, Ketones	OV-17, Carbowax 20M, SE-30
8a,b	Carboxylic acids	SP 1000
8c	Amides	Dexsil 300, Dexsil 400
8d	Esters	SE-30, OV-17
9	Nitriles	SP 1000
10	Amines	Carbowax 20M
11	Azo compounds, Hydrazines	-- 1
12	Nitrosamines	SE-30, SP 2100
13	Mercaptans, Sulfides, Disulfides	Carbowax 20M, SP 1000
14a.b	Sulfonic acids, Sulfoxides	SP 1000
15	Benzene and substituted benzenes	OV-17, SP 2100
16	Halogenated aromatic hydrocarbons	SE-30, OV-17, SP 2100, SE-54
17	Aromatic nitro compounds	OV-17
18	Phenols	SE-30 (FS)
19	Nitrophenols	SE-30 (FS)
20	Halophenols	SE-30 (FS)
21	Polynuclear aromatics	OV-17, SE-54, SE-30
22	Polynuclear aromatics	OV-17, SE-54, SE-30
23	Heterocyclic nitrogen compounds	OV-17, SE-54, SE-30
24	Heterocyclic oxygen compounds	SE-52, SE-30
25	Heterocyclic sulfur compounds	SE-52, SE-30, Carbowax 20M

FS - Fused silica column

1 - No capillary column recommended

APPENDIX C

MICROEXTRACTION

One of the methods recommended in the "Procedures for Level 2 Sampling and Analysis of Organic Materials," February, 1979 for preparing aqueous samples for analysis is exhaustive liquid/liquid extraction. The technique involves extracting one liter of an aqueous sample with 100 mL methylene chloride. The organic extract typically must be concentrated prior to analysis to achieve the desired sensitivity. The technique, recommended in the Level 2 report, for concentrating the extract uses a Kuderna-Danish evaporator fitted with a three-section Snyder column.

Microextraction[1,2] is suggested as a possible alternative to exhaustive extraction. Microextraction procedures usually involve a single equilibration of a 100 mL aliquot of an aqueous sample using sample-to-solvent ratios of 100:1 or higher. In other work at Arthur D. Little, Inc., the microextraction technique has been evaluated for the analysis of phenolic, aromatic, halogenated aliphatic and phthalate compounds. Some of the data from this work, as well as a brief description of the method, has been included in the appropriate method recommendations.

Exhaustive extraction is a useful technique because quantitative extraction may be approached even if the substances being extracted do not strongly favor the organic phase. However, this technique can be time consuming and relatively large volumes of aqueous sample are necessary. Further, it is usually necessary to concentrate the extract. The Kuderna-Danish technique is also time consuming and can introduce errors from losses of the analytes due to volatization.

On the other hand, microextraction is a rapid technique and uses small volumes of aqueous sample. Concentration of the extract is usually not necessary. This reduces volatization losses of the analytes, as well as eliminating interferences concentrated in the solvent. However, when using the microextraction technique for quantitative analyses, there are two major sources of variability. One is that the volume of the organic extract can be variable due to the solubility of the solvent into the aqueous phase and volatization losses. Secondly, since microextraction is performed at high sample-to-solvent ratios, compounds that do not partition strongly into the organic phase are less than completely extracted than they would if lower sample-to-solvent ratios were used.

These problems have been addressed at Arthur D. Little, Inc. and by Rhoades in several different ways. Variations in the solvent extract volume are limited by choosing a solvent with a low water solubility and by using an internal standard. Low recoveries are limited by saturating

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1. J. W. Rhoades and C. P. Nulton, "Priority Pollutant Analyses of Industrial Wastewaters using a Microextraction Approach," Env. Sci. and Health, Vol. 15, No. 6.

2. K. E. Thrun, K. Simmons and J. E. Oberholtzer, "An Evaluation of Factors Effecting the Microextraction of Benzene, Toluene, Ethyl Benzene and O-Xylene into Pentane" Env. Sci. and Health, Vol. 15, No. 6.

the aqueous samples with salt and by performing a parallel extraction and analysis of a spiked sample. Low recoveries from aqueous samples with suspended solids have been limited by extending the shaking time, and subsequently increasing the amount of contact between the sample and solvent. Further, the extraction of analytes, such as phenol with a partition coefficient of 28.8 (Log P = 1.46), has been improved by adjusting the pH$\leq$2.

Prior to the microextraction technique being used for sample preparation, a spiked field sample must be analyzed to determine if the technique is applicable and what, if any, modifications are necessary, such as extending the times for shaking the sample and extracting solvent. The following example illustrates how the microextraction procedure has been used to analyze phenols.

The pH of a thoroughly mixed aqueous sample was adjusted to less than 2 with 1:1 H_2SO_4:H_2O. A 90 mL aliquot of the pH ≤2 adjusted sample was transferred to a 100 mL volumetric flask containing 30 grams NaCl. A 5 µL aliquot of an internal standard solution (10 µg each o-bromophenol, 2,4-dibromophenol and p-benzylphenol in 1 mL methanol) was added to the sample. One mL of diisopropyl ether was added and the sample was shaken (inverted position) for 15 minutes using a wrist action shaker.

Aqueous samples (distilled, deionized water), to which phenols were added, were analyzed using this procedure. The experimental percent recovery data for four of the phenols added, as well as calculated recoveries from octanol:water partition coefficients, follow:

Compound	Log P*	Calculated Recovery 90:1	Experimental Recovery 90:1
2-Nitrophenol	1.79	41%	69%
Phenol	1.46	24%	54%
2,4,6-Trichlorophenol	3.06	93%	92%
4-Chloro-m-cresol	3.10	93%	92%
2,4-Dinitrophenol	1.54	28%	40%

*Octanol:water partition coefficient - Hansch, C. and Leo, J. J., "Substituent Constants for Correlation Analysis in Chemistry and Biology," Appendix II, Partition Coefficients, pp. 171-319, John Wiley and Sons, New Jersey, Copyright 1979.

The experimental data compare well with the calculated data. The improvement in recovery efficiency in the experimental data is probably due to the pH adjustment and subsequent suppression of the ionized species, salt saturation and use of an ether solvent.

APPENDIX D

CRITERIA FOR ELIMINATION OF WORST CASE DMEG VALUES

The decision criteria used to flag samples and/or compound categories for further analytical work are important factors in the transition from Level 1 to Level 2 in the phased approach to environmental analysis. In a Level 1 analysis, the collected data allow the identification of organic materials with boiling points greater than 100°C (TCO and GRAV ranges) by compound classes. However, the decision criteria, such as DMEG (MATE) values, are defined for specific organic compounds. Since, in general, it is not possible to identify individual chemical species within a given compound class from the Level 1 organic analysis data, estimates of the degree of hazard associated with an effluent stream are, at present, based on the most stringent DMEG (MATE) value for the category. In many cases, use of this "worst-case" DMEG (MATE) value does not represent an excessively stringent approximation. For example, the heterocyclic oxygen compound category has only one assigned DMEG (MATE) value, and the question of "worst case" approximation is, therefore, moot. There are other categories, however, for which a very large range of MATE values exist and for which using the most stringent criteria may lead to a substantial overestimation of the hazard of the effluent.

In some cases, the Level 1 organic analysis data, especially the LRMS results, provide sufficient information to allow one to rule out the presence of the compound with the worst case MATE value. Even though the specific compounds present in the sample are generally not identified, the absence of some particular compounds may be confirmed.

Tables D-1 to D-4 tabulate representative DMEG (MATE) values for several MEG categories listed in terms of increasing DMEG value within each compound category. Only TCO and GRAV range materials have been included in these tables since qualitative Level 1 data is generally obtained only for materials in these ranges. The DMEG (MATE) values tabulated are those for Air/Health; however, the DMEGs (MATEs) for other media would give the same order of worst case ranking except as noted in the tables. The tabulation has been carried down through compounds with progressively higher DMEG (MATE) values until a value within an order of magnitude of the highest MATE in the category is reached. This facilitates successive elimination of the more highly toxic species, or "looping".

In practice, the looping procedure involves looking at the data (or ranges) presented in the Level 1 organic analysis reports on a sample to see whether they are consistent with the identifying parameters of the worst case compound(s) listed in Tables D-1 to D-5. There are four generic types of inconsistency that could justify eliminating the worst case compound. They are:

1. LRMS results show the sample does not contain material in the MW range of the worst case compound. (i.e.,

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TABLE D-1

Identifying Parameters for Fused Aromatics, MW >216 (MEG 21, 22) Ranked by Increasing DMEG Value

Compounds with Worst Case DMEG Values			Identifying Parameters	
			LRMS	
COMPOUND	DMEG*	TCO/GRAV	MW	EL COMP
Benzo[a]pyrene	2×10^{-2}	GRAV	252	$C_{20}H_{12}$
Dibenz[a,h]anthracene	9.3×10^{-2}	GRAV	278	$C_{22}H_{14}$
7,12-Dimethylbenz[a]-anthracene	2.6×10^{-1}	GRAV	256	$C_{20}H_{16}$
3-Methylcholanthrene	3.8×10^{0}	GRAV	268	$C_{21}H_{16}$
Dibenzo[a,h]pyrene	4.3×10^{1}	GRAV	302	$C_{24}H_{14}$
Benz[a]anthracene	4.5×10^{1}	GRAV	228	$C_{18}H_{12}$
Benzofluoranthene	9×10^{2}	GRAV	252	$C_{20}H_{12}$
Dibenz[a]pyrene	1.1×10^{3}	GRAV	302	$C_{24}H_{14}$

Highest mate value in category is 2.7×10^{4} (Benzophenanthrene)

*Air, health basis; µg/m^3

TABLE D-2

Identifying Parameters for Fused Aromatics, MW <216 (MEG 21, 22)

Compounds with Worst Case DMEG Values			Identifying Parameters	
			LRMS	
COMPOUNDS	DMEG*	TCO/GRAV	MW	EL COMP
Phenanthrene	1.6×10^3	GRAV	178	$C_{14}H_{10}$
Dicyclopentadiene	1.6×10^4	TCO	132	$C_{10}H_{12}$
Methylphenanthrenes	3×10^4	GRAV	192	$C_{15}H_{12}$
Naphthalene	5×10^4	TCO	128	C_8H_{10}
Anthracene	5.6×10^4	GRAV	178	$C_{14}H_{10}$

Highest mate value in category is 2.3×10^5 (Alkyl Naphthalenes)

*Air, health basis; $\mu g/m^3$

TABLE D-3

Identifying Parameters for Heterocyclic Nitrogen Compounds (MEG 23)

Compounds with Worst Case DMEG Values			Identifying Parameters	
			LRMS	
COMPOUND	DMEG*	TCO/GRAV	MW	EL COMP
Dibenz[a,h]acridine	2.2×10^2	GRAV	258	$C_{21}H_{13}N$
Dibenzo[c,d]carbazole	1×10^3	GRAV	267	$C_{20}H_{13}N$
Pyrrole	2.7×10^3	TCO	67	C_4H_5N
Benzothiazole	4.3×10^3	TCO	135	C_7H_5NS
Methylbenzothiazoles	4.7×10^3	TCO	149	C_8H_7NS
Chloropyridine	4.8×10^3	TCO	113	C_5H_4NCl
Benz[c]acridine	1.1×10^4	GRAV	229	$C_{17}H_{11}N$

Highest mate value in category is 9×10^4 (Acridine)

*Air, health basis; $\mu g/m^3$ For aqueous or solid media, the ranking of the first two compounds is reversed; Dibenzo[c,d]carbazole has a lower MATE than dibenz[a,h]acridine.

TABLE D-4

Identifying Parameters for Heterocyclic Sulfur Compounds (MEG 25)

Compounds with Worst Case DMEG Values			Identifying Parameters	
			LRMS	
COMPOUND	DMEG*	TCO/GRAV	MW	EL COMP
Benzonaphthathiophene	9.9×10^2	GRAV	234	$C_{16}H_{10}S$
Methylthiophenes	2.3×10^4	TCO	98	C_5H_6S
Benzo[b]thiophenes	2.3×10^4	TCO	134	C_8H_6S

Highest mate value in category is 2.3×10^4 (Benzo[b]thiophenes) .

*Air, health basis; μg/m^3

Organics in the sample are either all lower MW or all higher MW than the worst case compound).

2. Sample organics are all GRAV range while worst case compound is in TCO range (or vice versa).

3. LRMS results show that the elemental composition range of organics in the sample is not compatible with the worst case compound. (i.e., no polyhalogenated compounds are found).

4. Sample has no IR absorbance in region where worst case compound has distinctive, strong absorbance. (e.g., nitro group in nitrophenols).

As an example of how the decision criteria just stated may be used to determine the appropriate DMEG value to be applied to the estimation of the degree of hazard associated with a specific environmental sample, consider the following. The results of a Level 1 analysis show that a stack gas sample includes:

a) 100 $\mu g/m^3$ of fused aromatics with molecular weight >216 with molecular weights between 216 and 250.

b) 10^3 $\mu g/m^3$ of phenols consisting of nonyl phenol.

All of the Level 1 reported levels exceed the worst case DMEG for their appropriate MEG category. To determine whether or not the worst case DMEG value should be used to designate the degree of hazard for the source of this sample, the looping method described above should be used for these two categories.

Table D-1 shows the worst case DMEG values for the fused aromatics with MW >216 category. The worst case value from this table is 2×10^{-2} $\mu g/m^3$ for benzo(a)pyrene, which is much lower then the Level 1 reported level of 1×10^2 $\mu g/m^3$. However, the Level 1 reported molecular weight range for this category in the sample is lower than that of benzo(a)pyrene. Thus, use of the benzo(a)pyrene worst case value is eliminated in the looping process and the next worst case DMEG compound is considered (dibenz(a,h)anthracene). The entries of this table are sequentially eliminated due to their molecular weights until the entry for benz(a)-anthracene is encountered. At that point, the looping procedure is stopped since there is no grounds for the elimination of benz(a)anthracene. At this point, an upper limit estimate for the discharge severity of the source of this sample may be computed, and that informtion used to determine what further action should be taken for this sample.

For the phenols category, a similar looping procedure would be undertaken (see Table D-5). Since the compound identified by Level 1 methods does not contain either nitro groups or halogens, the worst case values for MEG Category 19 - halophenols (pentachlorophenol with DMEG = 5.0×10^2 $\mu g/m^3$)

TABLE D-5

Worst Case DMEG Values for Phenols (MEG 18, 19, 20)

Category	Compound	DMEG*
20	Trinitrophenol	1.0×10^2
19	Pentachlorophenol	5.0×10^2
18c	β-Naphthanol	1.1×10^5
18b	1,4-Dihydroxybenzene	2.0×10^3
18a	2,2'-Dihydroxydiphenyls	6.8×10^3
18a	Polyalkyl phenols	1.5×10^4

*Air, health basis; μg/m^3

and MEG Category 20 - nitrophenols (trinitrophenol with DMEG = 1.0×10^2 μg/m^3) are eliminated. Similarly, the worst case DMEG values for MEG Category 18b (dihydric and polyhydric phenols) and MEG Category 18c (fused ring hydroxy compounds) are also eliminated on structural grounds. Since nonyl phenol is a mixture of C_9 substituted phenols, the DMEG value for polyalkyl phenols (1.5×10^4 μg/m^3) is appropriate to this sample. The nonyl phenol level (1×10^3 μg/m^3) is lower than the appropriate DMEG value, hence no further action needs to be taken for this compound.

APPENDIX E

LIMITS OF DETECTION FOR LEVEL 2 SAMPLING

The limit of detection for specific compounds in Level 2 studies depends upon two factors - the instrumental detection limit for that compound and the concentration steps taken during sample preparation. In the following discussion, limits of detection for a hypothetical compound will be derived for the major types of samples - gaseous, liquid and solid - likely to be encountered during Level 2. For the purposes of this discussion, the instrumental detection requirements will be assumed to be constant, and the specific instrumental requirements will be the analysis of a 1 μL of a 1 ng/μL solution of the hypothetical compound in a suitable solvent. The assumptions made to allow derivation of the limits of detection in various media are summarized in Table E-1.

The derived limits of detection may be scaled up to the specific data for real compounds by adjusting the instrumental factors of the analysis volume and analysis concentration. That is, if the specific instrument limit of detection for compound X is 10 ng total and the maximum sample size for the instrument is 2 μL (these factors are equivalent to an instrumental detection limit of 5 ng/μL for a 1 μL sample aliquot), then the limit of detection for compound X in the original sample is 5 times that derived herein and reported in Table E-2.

Gaseous Samples

Gaseous samples for Level 2 studies will be collected by either SASS or modified Method 5 sampling trains. Under typical operating conditions, a SASS sample represents 30 m^3 of stack gas while a modified Method 5 sample represents about 5 m^3 of stack gas. The following discussion treats gaseous samples collected by SASS trains. An analogus treatment could be presented for modified Method 5 train samples with the difference in the limit of detection for the two methods resulting primarily from the difference in the volume of gas samples. The results derived in this treatment are for the total sampling train; it is assumed that the appropriate liquid and solid extracts have been combined prior to any LC steps.

Sample work up for Level 2 samples is conveniently performed through Level 1 clean up and extraction procedures. Hence, a 30 m^3 SASS-collected gas sample is prepared through several extraction steps and concentrated to 10 mL. The concentrated extract is partitioned into four aliquots, of which 1 mL is used for GRAV determination, 0.005 mL for TCO determination, 1-8 mL for LC separation depending on the sample level and the remainder reserved for dealing with any potential problems. Following solvent exchange into pentane, the Level 1 LC procedure separates the sample aliquot into 7 fractions with volumes of 25 mL for LC fraction 1 and 10 mL for each of the remaining LC fractions 2 through 7. If the compound of interest is distributed between several LC fractions, portions of the relevant LC fractions may be combined. Depending upon the amount

TABLE E-1

Assumed Parameters for Computation of Limits of Detection

Parameter	Assumption
Instrumental Requirements	1 μL of the LC sample at a level of 1 ng/μL (1 μg/mL)
Sample Extract Amount*	10 mL
Sample Extract Used for LC*	8 mL
Distribution of Component	Found in 2 LC fractions which were combined (20 mL total)
Concentration Factor for Combined LC Fractions	10
Extraction Efficiency	100%

*Not used in limit of detection computation for neat organic liquid

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TABLE E-2

Limits of Detection for Level 2 Environmental Samples

	Sample Size	Limit of Detection
A. Gases		
1) SASS train	30 m^3	0.08 μg/m^3
2) Modified Method 5	5 m^3	0.50 μg/m^3
B. Liquids		
1) Aqueous Samples	10 L	0.25 μg/L
2) Neat Organic Liquids	0.10 g	20 μg/g
C. Solids	100 g	0.025 μg/g

Note: Limits of detection stated are for a single component which is distributed between two LC fractions. It is assumed that the instrumental detection limit for the component is 1 μg/mL, the sample extract was reduced to 10 mL prior to LC, 8 mL of the extract was taken for LC and the two combined LC fractions could be reduced in volume by a factor of 10. Limits of detection were calculated via the equation:

$$\text{LOD} = (\text{instrumental detection limit in terms of conc.}) \times \left(\frac{1}{\text{conc. factor}}\right) \times (\text{total volume of combined LC fractions})$$

$$\times \left(\frac{\text{total amount of sample extract}}{\text{amount of sample extract used for LC}}\right) \times \left(\frac{1}{\text{original sample size}}\right)$$

of material present in the LC fractions, the volume of the LC eluent may be reduced prior to analysis with a concentration factor of between 2 and 10 normally possible.

For the following derivation, the amount of stack gas samples is assumed to have been 30 m^3. Using this assumption and the conditions of Table E-2, the detection limit in the stack gas is computed as follows:

A) The concentration of material X in the concentrated LC effluent is 1 ng/μL = 1 μg/mL.

B) The concentration in the LC effluent originally is 1/10 (1/concentration factor) of the analyzed concentration (i.e., if 5 mL of LC 3 is added to 5 mL of LC 4 and reduced to 1 mL to give a 10X concentration of the LC fraction, then the 1 ng/μL level of Step A is equivalent to 0.1 ng/μL of compound X in the combined LC fractions.

C) The amount of X in the LC fractions is 20 times that of Step B.

D) Since the amount of X present in the LC fractions is only 8/10 that of the original extract (volume taken for LC/volume of extract), the amount of X in the sample is 10/8 that of Step C.

E) Since the gas sample volume was originally 30 m^3, the limit of detection of X in the stack gas is the amount of X from Step D divided by the 30 m^3 gas volume.

Thus, the limit of detection (LOD) for compound X in the stack is:

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$$\text{LOD} = (\text{instrumental LOD in terms of concentration}) \times \left(\frac{1}{\text{conc. factor}}\right)$$

$$\times\ (\text{volume of LC eluent}) \times \left(\frac{\text{amt. of extract}}{\text{amt. used for LC}}\right) \times \left(\frac{1}{\text{volume of stack gas}}\right)$$

$$= (1\ \mu\text{g/mL}) \times \left(\frac{1\ \text{mL}}{10\ \text{mL}}\right) \times (20\ \text{mL}) \times \left(\frac{10\ \text{mL}}{8\ \text{mL}}\right) \times \left(\frac{1}{30\ \text{m}^3}\right) = 0.08\ \mu\text{g/m}^3$$

Liquid Samples

Two types of liquid samples may be encountered during Level 2 studies, aqueous samples, such as process water, or organic liquids, such as the

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combined residues from several chemical reactions. The derivation of limits of detection for these two types of liquids will be presented separately in the following discussion.

For aqueous samples, a 10 L aliquot of the sample is serially extracted with methylene chloride. The methylene chloride is concentrated and prepared in an identical fashion as was presented for gaseous samples. If the volume of aqueous sample extracted was 10 L, then using the volumes of Table E-2 the limit of detection for the compound of interest in this sample is:

$$\text{LOD} = \left(\frac{1\ \mu\text{g}}{\text{mL}}\right) \times \left(\frac{1\ \text{mL}}{10\ \text{mL}}\right) \times (20\ \text{mL}) \times \left(\frac{10\ \text{mL}}{8\ \text{mL}}\right) \times \left(\frac{1}{10\ \text{L}}\right)$$

$$= 0.25\ \mu\text{g/L of aqueous sample}$$

For organic liquid samples, there is no sample extraction prior to LC separation. A 100 mg aliquot of the sample is applied directly to the LC column (if the organic liquid is completely soluble in cyclopentane, the 100 mg aliquot may be dissolved in cyclopentane for ease of transfer) and then fractionated by Level 1 methods. If the amount of organic liquid taken for LC was 100 mg, then the limit of detection for the component of interest in the organic liquid is:

$$\text{LOD} = \left(\frac{1\ \mu\text{g}}{\text{mL}}\right) \times \left(\frac{1\ \text{mL}}{10\ \text{mL}}\right) \times (20\ \text{mL}) \times \left(\frac{1}{0.100\ \text{g}}\right)$$

$$= 20\ \mu\text{g/g of organic liquid}$$

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Solid Samples

Solid samples, whether particulate, resin, sediment, etc., are treated similarly within the context of Level 2. Some portion of the sample, 20 g - 500 g, will be Soxhlet extracted with methylene chloride. The extract will be processed via Level 1 methods as described previously for gaseous and liquid samples. The limit of detection for a component in a solid sample is computed in an analogus fashion to those limits of detection described previously. If the amount of solid sample extracted was 100 g, then the limit of detection for the compound of interest in

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this solid is:

$$\text{LOD} = \left(\frac{1\ \mu\text{g}}{\text{mL}}\right) \times \left(\frac{1\ \text{mL}}{10\ \text{mL}}\right) \times (20\ \text{mL}) \times \left(\frac{10\ \text{mL}}{8\ \text{mL}}\right) \times \left(\frac{1}{100\ \text{g}}\right)$$

$$= 0.025\ \mu\text{g/g of solid sample}$$

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